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The Science of Chemistry



Underwater explosion of an atomic bomb
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The Science of Chemistry

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FIRST EDITION

McGRAW-HILL BOOK COMPANY, INC.

NEW YORK TORONTO LONDON 1949

THE SCIENCE OF CHEMISTRY

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Preface

OVER a period of approximately ten years the authors of the present volume have accumulated, separately and collectively, a rather considerable experience in instruction in so-called "terminal" courses in chemistry. During this time there has been provided the opportunity for a careful evaluation of the whole problem of the needs of students who specialize in non-technical areas but who are required (or less frequently elect) to devote at least a minimum period to the study of one or more of the physical or biological sciences. This experience has also provided occasion for consideration of the obligations of the departments and teachers who offer such courses.

The composite viewpoint that is reflected in the following pages is influenced also by a knowledge of instructional methods and outlooks that prevail elsewhere. Another contributing factor is the matter of course content as reflected by the textbooks that are available for use in terminal courses.

It seems clearly evident that due recognition must be given to the fact that courses of the type in question are not to be considered as prerequisite to any further study of the subject. This fact alone bespeaks a degree of latitude in choice of subject matter and emphasis that is only infrequently encountered and less frequently exploited to best advantage. One must not permit the terminal course to be no more than a truncated version of the conventional general chemistry course. Such is all too commonly the case, and this situation usually leads to an inappropriate distribution of emphasis. For example, far too little time is spent on organic and biological chemistry, familiar industrial and commercial applications of common chemicals, economic considerations, etc.

The terminal course, on the other hand, should not be permitted to become a diffuse collection of purely descriptive and factual material. Sufficient emphasis must be placed upon fundamental principles

to bring the scientific method into proper perspective and to provide a basis for at least a reasonable amount of laboratory work. It is a continuing conviction that the non-technical student cannot achieve anything approaching a proper appreciation of an experimental science without an active participation in laboratory study.

Finally, it seems clear that the major problem of the terminal course is one that must be faced not by the student but rather by the teacher. Either as a result of habit acquired in the teaching of general chemistry courses or because of misdirected enthusiasm, too many teachers are unwilling to adjust their approach to the task at hand. Students who take the terminal course in chemistry are not potential chemists and need not be indoctrinated with the significance of deviations from Raoult's law or the intricacies of the synthesis of quinine. The teacher who is unwilling to deviate from the more rigorous approach renders a disservice to his students, to himself, and to his chosen field of interest. Some who may examine the content of this volume will no doubt be pained to note the omission of the traditional discussion of, for example, the law of multiple proportions and the derivation of combining weights. The authors feel that the burden of the proof rests with those who espouse the inclusion of these and similar items as part of the subject matter of the terminal course.

The authors wish to express their gratitude to all of those who aided in the procurement of illustrative materials. Especial thanks are due Eva V. Armstrong, Curator of the Edgar Fahs Smith Memorial Collection in the History of Chemistry, of the University of Pennsylvania.

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AUSTIN, TEX.

March, 1949

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Historical Introduction

IN AN ERA that has witnessed the development of the atomic bomb, jet-propelled aircraft, guided missiles, bacteriological warfare, and other devices for mass destruction, one may reflect with considerable profit upon the words of the Roman philosopher Pliny (A.D. 23-79). In his "Natural History," Pliny wrote as follows:

It is by the aid of iron that we construct houses, cleave rocks, and perform so many other useful offices of life. But it is with iron also that wars, murders, and robberies are effected, and this, not only hand to hand, but from a distance even, by the aid of weapons and winged weapons, now hurled by the human arm, now launched from engines, and now furnished with feathery wings. This last I regard as the most criminal artifice that has been devised by the human mind; for, as if to bring death upon man with still greater rapidity, we have given wings to iron and taught it to fly. Let us, therefore, acquit Nature of a charge that belongs to man himself.

Thus it is evident that many of the socio-political and moral issues that attend consideration of modern scientific developments are not so new as many would have us believe. Apparent also is the fact that the impact of science upon civilization must have had its origin in periods that antedate recorded history. One may therefore justifiably adopt the view that the cultural contributions of the more exact sciences may be traced to best advantage and evaluated most objectively in relation to their contemporary history. Such will be one of the purposes of the paragraphs that follow.

The Ancient Arts. The emergence of chemistry as a true science cannot be specified in terms of any exact date. At best, one may do no more than designate a period—and that in only ill-defined terms. Numerous lines of evidence, however, show that the evolution of chemistry included certain very early practices that are worthy of consideration only as arts or crafts. Many clues to the probable status of these early chemical arts may be gleaned from statements in the Bible.

Information also arises from the study of the earliest of man's writings, but these are often extremely difficult of interpretation. Still other indications are based upon archaeological discoveries, but these are frequently clothed in temporal uncertainty.

Despite all of these uncertainties, it is well established that the



Figure 1. An early use of a common metal is illustrated by the lead roofs installed on St. Sophia, Istanbul, between A.D. 532 and 537 (Courtesy Lead Industries Association.)

manufacture and use of glass, pottery, dyes, etc., were common practices in prehistoric times. Reference to products such as vinegar and alcoholic beverages (wine in particular) are to be found in the Old Testament. Gold ornaments of the Stone Age establish this metal as probably the one first known to man, and both gold and silver are mentioned frequently in the Bible. For a long time, silver was considered more precious than gold. In the book of Genesis, it is recorded that Abraham bartered silver for a burial place for Sarah. Copper and antimony were known as early as 3000 B.C. and mercury approximately by 1500 B.C. The metals lead, tin, and iron were also known to

ancient man, and it appears that articles made of bronze were in use as early as 2500 B.C. The early Romans fabricated water pipes of lead and, incidentally, made the grievous error of fashioning cooking utensils of this same metal. It seems highly probable that this latter practice led to the premature demise of many a stalwart Roman as a result of lead poisoning. Steel was probably in use prior to 1000 B.C. Of the non-metallic substances, carbon was most certainly known in prehistoric times in the form of soot and charcoal, and the Bible contains reference to another form of carbon, the diamond. Sulfur, referred to in the Bible as "brimstone," was early used as a medicine and for a variety of other purposes.

Whatever may have been the state of development of these early arts and crafts, knowledge concerning them was perpetuated only as it was passed verbally from one generation to another. These crafts were the province of illiterate artisans. Those who were capable of independent thought and the preparation of written records were apparently unacquainted with the practical arts and uninterested in an experimental approach. For example, Aristotle stated that a barrel full of ashes will hold as much water as an empty barrel. Apparently it never occurred to either Aristotle or any of his contemporaries to perform the obvious experiment in an effort to confirm or disprove the statement. Social distinctions of those times permitted no common meeting ground for the artisan and the philosopher, whose position was one of dignity and whose efforts were restricted to processes of pure thought. It is a remarkable fact that this aggrandizement of the purely mental and the disdain of manual labor were more or less prevalent throughout the succeeding centuries and are far from unknown in our modern society. As late as the sixteenth century, teachers of anatomy considered dissection as unworthy of their exalted position. The task was commonly performed by barbers while the teachers offered more or less appropriate explanations. In this state of affairs there is certainly reflected a philosophical influence upon the progress of science, and one is tempted to speculate whether it might not also account for certain tendencies occasionally exhibited by the present generation of barbers.

In any event, the net result of this sharp segregation of theory and practice was a period of little progress, at least so far as the chemical arts were concerned. Much more significant progress was made in the

more abstract areas of learning such as metaphysics, mathematics, and astronomy. More rapid strides along chemical lines were destined to await a clear recognition of the value of experimentation.

Alchemy. From these fragmentary beginnings in ancient times, it



Figure 2. An alchemical laboratory. (Photograph of a reconstruction formerly in the Deutsches Museum.) (Courtesy of the Edgar F. Smith Memorial Collection, University of Pennsylvania.)

is not to be anticipated that the Middle Ages could have contributed much toward real progress. Particularly during the decline of the Roman Empire, there was a decidedly downward trend in accomplishment in all intellectual pursuits. To a limited extent accomplishment was possible in literature and philosophy, since these fields enjoyed the tolerance if not the unlimited approval of the Church.

Nevertheless, the period from A.D. 500 to 1400 is significant, be-

cause it witnessed the rise of alchemy. The etymology of the term provides a clue to certain characteristics of the activities included within its scope; *i.e.*, alchemy was commonly referred to as "the Egyptian black art." Despite this implication as to its origin, there is other evidence that alchemy was practiced early in China and may actually have originated there.

Since the writings of the alchemists are so intertwined with mysticism, superstition, religious ritual, and apparently deliberate efforts at concealment, all of the objectives of the alchemists cannot be deduced from their rather unintelligible ramblings. Even so, it seems clear that the main objective was to transform the base metals (*e.g.*, lead, iron, etc.) into gold. As a means of accomplishing this end, the alchemists sought some sort of *materia prima*, which is commonly referred to as the *philosopher's stone*. It was believed that this mysterious and all-powerful something would not only turn other metals into gold, but would cure all human ills, endow its discoverer with riches and supernatural qualities, and perform many other wonders. This philosopher's stone was sought in almost every imaginable material source and with a zeal that is to be admired for its fervor if not for its rationality. Jaffe gives an interesting if possibly somewhat imaginative account of the alchemist Bernard Trevisan

... in the act of hardening two thousand hens' eggs in huge pots of boiling water. Carefully he removes the shells and gathers them into a great heap. These he heats in a gentle flame until they are white as snow, while his co-laborer separates the whites from the yolks and purifies them all in the manure of white horses. For eight long years the strange products are distilled and redistilled for the extraction of a mysterious white liquid and a red oil.¹

Needless to add, neither proved to be the philosopher's stone, but the failure of this experiment doubtless did little to deter Trevisan from concocting other equally strange products by even stranger processes.

No account of alchemy would be complete without recognition of some of the practices that it spawned. The very fact that gold was an objective suggests the possibility of chicanery. Indeed, the history of alchemy is replete with examples of fraud, trickery, and deception of a high order. Various alchemists at one time or another claimed to

¹ Reprinted from "Crucibles" by permission of Simon and Schuster, Inc., publishers. Copyright, 1930, by Bernard Jaffe.

have made the great discovery, and many a gullible citizen was separated from his savings account after having witnessed a spurious but cleverly conducted "demonstration." Such swindles must have been common. It is said that Frederick of Würzburg provided a special gallows that was reserved for alchemists, and as late as 1404 the English Parliament passed an act forbidding the production of gold by alchemical methods. Henry VI, however, was more astute. He not only permitted but openly encouraged such efforts since he perceived therein a possible means of absolving an embarrassing indebtedness.

Despite these and other characteristics, the alchemical period was not without its accomplishments. Many new and useful substances were discovered—by accident to be sure, but these discoveries loom large to the extent that they foreshadowed far more significant events. The weird practices of alchemy brought to light materials such as arsenic, sulfuric acid, borax, plaster of Paris, etc. In addition, numerous articles of equipment and several common laboratory processes and procedures had their origin in that distant period. Judged in terms of twentieth-century standards, the yield of new knowledge was indeed meager in relation to the magnitude of the effort expended. On the other hand, perhaps the same may come to be said of twentieth-century progress after the lapse of a comparable interval of time.

Iatrochemistry. Alchemy came by no means to an abrupt end. The search for the philosopher's stone continued on an abated scale while new motivations appeared on the horizon. Realization of the alchemist's dream of transformation of other metals into gold was destined to await, and become an accomplishment of, twentieth-century science.

The revival of learning that began in the fourteenth but became more evident in the fifteenth century set the stage for the evolution of chemistry as a true science. Within the period from A.D. 1400 to 1700, a single development overshadowed all others. It was in this interval that the *experimental method* came to occupy a position of prime importance. No longer were statements of those philosophically inclined so likely to be accepted as fact without any effort at verification. Those who worked with their hands began to think for themselves; they evolved theories (albeit crude ones), and it actually became respectable to perform at least certain types of experiments.

Early in this period the search for the philosopher's stone was

progressively replaced by the quest for the *elixir of life*. Many alchemists and physicians alike turned their attention to the search for a universal medicine, which they believed would not only cure all of the ills of mankind but also restore youth to the aged and prolong life so that man could live for hundreds of years. This suggests a close interrelationship of chemistry and medicine, and indeed the histories of the two throughout the period in question are scarcely distinguishable. The practice of medicine in that time was based largely upon the teachings of the early Greek physicians Galen (A.D. 130–200?) and Hippocrates (460–359 or 377? B.C.) and consisted in the treatment of ills by methods that now seem little short of barbaric. Despite the fact that the teachings of Galen and Hippocrates were steeped in superstition and unverified by experiment, their influence was most profound. The solemn oath taken by those who are today about to embark upon a career in medicine and that is supposed to define a standard of professional ethics is known as the Hippocratic Oath, in deference to the “Father of Medicine.”

Reform in medicine and a new impetus in chemistry were paralleled by other evidences of a rebirth of intellectual activity. The invention of printing by Johannes Gutenberg stimulated writing and the exchange of information and ideas in a degree hitherto impossible. The discovery of the new world by Christopher Columbus in 1492 was another evidence of that brand of curiosity that makes for progress. The Protestant Reformation had its origin in this same period, when Martin Luther nailed his ninety-five theses on the door of the Castle church in Wittenberg in 1517. At about the same time Copernicus came forth with the novel conclusion that the sun, and not the earth, is the center of the physical universe. This was indeed a period of renaissance.

Much of the improved outlook in chemistry and medicine was due to the activities of a character called Paracelsus (1493–1541) but whose full name was Philippus Aureolus Paracelsus Theophrastus Bombastus Eremita von Hohenheim. Vain, vitriolic, and vulgar of speech, Paracelsus throughout his lifetime waged a one-man war for reform in medicine and heaped condemnation upon the physicians and apothecaries who subscribed to the witchcraft of Galen and Hippocrates. Merely to record that Paracelsus was hated by most of the physicians of his time is a gross underestimate. He described the current

remedies and prescriptions as “foul broths” and to the physicians he said, “You are not worthy that a dog shall lift his hind leg against you.”

Paracelsus was probably the first to recognize that life processes are



Figure 3. Philippus Aureolus Paracelsus. This is a photograph of a woodcut believed to be the first exact portrait of Paracelsus. (Courtesy of the Edgar F. Smith Memorial Collection, University of Pennsylvania.)

fundamentally chemical. He strove for the application of chemicals to medicine, and his efforts led to vast improvement in the methods for the treatment of disease. He was the first to use preparations containing mercury, he introduced to medicine the use of opium (which he called *laudanum*), and he initiated many other remedies that are still in use, for example, medicinals containing arsenic, copper, and lead. Of more far-reaching importance, however, was his contribution to the evolution of the experimental approach to the solution of all kinds

of problems. Almost unaided he forced upon men of his time a realization of the value of experimentation, and for this alone all science and all mankind owe to him an immeasurable debt of gratitude. His viewpoint is clear from the following quotation from his writings:

I admonish you not to reject the method of experiment, but, within the limits of your abilities, follow it without prejudice. Every experiment is like a weapon which must be used according to its particular virtue, as a spear to thrust, a club to strike; so also is it with experiments.

It is not without basis that one may hazard the guess that were it not for the influence of this fifteenth-century crusader the progress of science might have been impeded for hundreds of years.

These and other developments during the renaissance period were destined to give birth to chemistry as a science worthy of the name. Still more notable contributions were made during the latter part of the seventeenth century. Among these were the discovery of the barometer by Torricelli in 1643, the discovery of the laws of gravitation by Newton in 1665, the invention of logarithms by Napier in 1614, and Robert Boyle's classical work on the properties of gases and in other phases of physical and chemical science. So revolutionary were the effects of Boyle's discoveries that he is often referred to as the father of modern chemistry. By the beginning of the eighteenth century, the sciences were truly on the threshold of momentous events; chemistry was about to come of age.

Chemistry in the Eighteenth Century. The chemical science of the early eighteenth century is perhaps more aptly described as chemical philosophy. Many phenomena that are today considered simple and elementary were incorrectly interpreted and incompletely understood. Wholly different interpretations, for example, were given to the nature of fire and the process of combustion. The nature and constitution of the atmosphere and of simple materials such as water were unknown. The infant science of chemistry was still impeded by an inheritance of vague and contradictory ideas that were destined to persist for nearly a century. It had become, however, a truly experimental science, and therein lay the key to progress. Out of this thick fog of confusion there arose in the latter part of the eighteenth century the first real evidence of orderliness; even the language and terminology of chemistry showed signs of systematization.

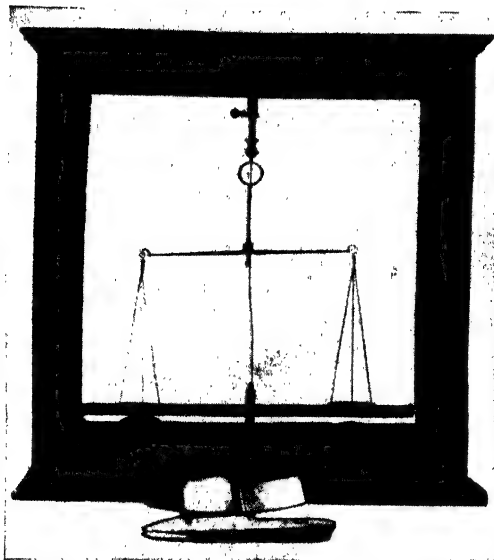


Figure 4. An early balance used by Joseph Priestley and now the property of the Pennsylvania State College. (*Courtesy of the Edgar F. Smith Memorial Collection, University of Pennsylvania.*)

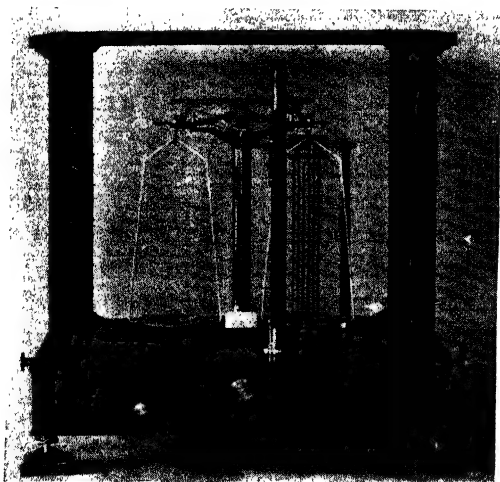


Figure 5. A modern balance. (*Courtesy of Wm. Ainsworth and Sons, Inc.*)

The period that gave birth to the French Revolution and saw it brought to fruition witnessed also something akin to a revolution in chemical thought. Although many contributed to this new order in science, a few names and accomplishments are particularly worthy of note. The English clergyman Joseph Priestley (1733–1804) turned his attention to science when his religious views brought him into popular disfavor. He is credited with the independent discovery of oxygen and contributed much to the development of improved methods for the conduct of a wide variety of chemical experiments. Incidentally, he was the first to prepare what is now known as “soda water.” He was a contemporary and friend of the Scotch engineer James Watt, who invented the first practical steam engine. Both before and after he came to America in 1794, Priestley conferred on various occasions with Benjamin Franklin. Priestley was also a friend of George Washington, and of Thomas Jefferson, who once sought Priestley’s advice on matters relative to the establishment of the University of Virginia.

Another notable English scientist of this period was Henry Cavendish (1731–1810), an eccentric and unpretentious man of great wealth who was descended from a family noted for its accomplishments in affairs of state. A recluse and a woman hater, Cavendish found no appeal in politics and devoted his life to the study of the natural sciences. Among his many discoveries, that of hydrogen is the one for which he is best known. His work was particularly characterized by his devotion to *accurate measurements* and by his clear recognition of their importance. In this view he was joined by the French aristocrat, scientist, and social reformer Antoine Laurent Lavoisier. Lavoisier presented the first clear picture of the process of combustion; he invented and perfected the first chemical balance worthy of the name



Figure 6. Antoine Laurent Lavoisier. (Courtesy of the Edgar F. Smith Memorial Collection, University of Pennsylvania.)

and thus promoted the accurate determination of weights and laid the foundation for precise chemical analysis. He was the first to introduce systematic chemical nomenclature and wrote the first textbook of chemistry. Not for this, but rather because of his close association with matters political he was beheaded at the guillotine in 1794. He was collector of taxes. Lavoisier was a contemporary of the distin-



Figure 7. Apparatus used by Lavoisier. (Courtesy of the Edgar F. Smith Memorial Collection, University of Pennsylvania.)

guished botanist Linnaeus, the noted French astronomer Laplace, and the political leader Pierre du Pont de Nemours, who, like Priestley, emigrated to America and founded the company that still bears his name.

It shall not be the purpose here to chronicle the orderly sequence of subsequent developments. So fundamental were many of the discoveries that there will be ample occasion to refer to them at appropriate places in the chapters that follow.

What Is Chemistry? The foregoing and all too brief account of the

evolution of chemical science is at least sufficient to reflect a progressive change in viewpoint. It should also serve to focus attention upon some of the materials that occupy the attention of the chemist. In time, chemists came to interest themselves in essentially every kind of object in the ever-changing material universe, in the air, the earth, the seas, and all that they encompass. They came to study living as well as inanimate objects and to concern themselves with every conceivable change that occurs and with the reasons for these changes.

The stages in the development of chemistry may be epitomized in terms of three questions. Initially, man was content to ask, *What?*, an inquiry that was only slowly replaced by the questions, *What and how much?* Chemistry was not to become a true science, however, until to these was added the still more important question, **Why?**

Accordingly, we may state that *chemistry is the branch of physical science that is concerned with the nature and composition of matter, with the changes which it undergoes, with the related energy changes, and more particularly with the reasons for these changes.* Because chemistry is only one of many sciences, it seems worth while next to consider its relationship to other sciences as well as to other less closely related areas of learning.

COLLATERAL READING

The list of references at the end of each chapter is provided for the use of those who would read and study more extensively some of the topics covered only briefly in this book. In most, although not in all cases, reference is made to monographs and textbooks somewhat more advanced than the present volume.

THORPE: "Essays in Historical Chemistry," The Macmillan Company, London, 1894.

VENABLE: "A Short History of Early Chemistry," D. C. Heath and Company, Boston, 1896.

LOWRY: "Historical Introduction to Chemistry," The Macmillan Company, London, 1915.

REDGROVE: "Alchemy: Ancient and Modern," W. Rider and Son, London, 1922.

ARMSTRONG: "Chemistry in the Twentieth Century," Longmans, Green & Co., Inc., New York, 1924.

STILLMAN: "The Story of Early Chemistry," Appleton-Century-Crofts, Inc., New York, 1924.

MOORE: "History of Chemistry," McGraw-Hill Book Company, Inc., 1st ed., New York, 1931.

DAMPIER: "History of Science," The Macmillan Company, New York, 1932.

BERRY: "History of Modern Chemistry," Cambridge University Press, London, 1946.

The Relation of Chemistry to Other Fields of Knowledge

FROM the preceding discussion it is evident that the development of the chemical arts and sciences had a profound influence upon the whole field of medicine and the healing arts. This influence was by no means unilateral. Progress in medicine made for progress in chemistry and in related fields. Similarly, advances in numerous other areas of learning had at least some bearing upon progress in chemistry, and vice versa.

It shall be the purpose of this chapter to show in true perspective the position of chemistry relative to the other sciences, and more broadly to all fields of knowledge. To those who are particularly interested in any given subject, its influence and importance loom large and are not infrequently exaggerated. We shall attempt here to show how chemistry fits into the over-all pattern, the manner in which it and other subjects are interrelated, and something of the extent to which the science of chemistry influences our everyday lives. At the same time, it is to be understood that much that is said here concerning chemistry may be said with comparable validity concerning other subjects.

The Classification of Knowledge. This topical heading sounds like a large order—and indeed it is. Whenever one who is unaccustomed to thinking broadly in terms of the sum total of mankind's accumulation of knowledge considers the problems that its organization and classification present, the task seems almost insurmountable. Philosophers have pondered over the problem, have written volumes about it, and have remained dissatisfied with the results of their efforts.

Nevertheless, an appreciation of the status of the science of chemistry in relation to all other sciences and their place in the larger domain

requires at least a necessarily brief effort at orientation. One of the better and more concise classifications is that given by Bliss and essentially reproduced in Table 1. This table comprises four columns, the first of which lists the various branches of philosophy. The parallel fields of science are given in the second column and the related historical studies in the third. The corresponding applied sciences, technologies, and arts (practical and otherwise) constitute the fourth and final column. This table should be read from left to right in order to see clearly how the various fields of knowledge are interrelated. Finally, it should be noted that subdivision into successive columnar listings does not imply *separation* or lack of interdependence.

It is inevitable that this or any other equally ambitious undertaking should lead to disagreement, particularly with respect to details. It may be argued, for example, that Bliss's classification is not adequately subdivided and that some fields are improperly classified. One may choose, for instance, to ally mineralogy (and crystallography) with geology rather than chemistry, and yet the close relationship to both of these sciences—and to physics—is undeniable. It seems worth while also to point out that the various phases of engineering are included by implication rather than specific designation. The same is true of pharmacy, and a few other fields.

Whatever system of classification is adopted, one must remember that the compartmentalization of knowledge is an artificiality born of the necessity for convenience. All of the various areas of human endeavor are in some degree interrelated and interdependent. Perhaps this fact can be made more evident by an examination of the status of a few of the sciences relative to each other.

The Physical and Biological Sciences. If, now, we may segregate a few of the sciences and their applications, it becomes somewhat simpler to show areas of mutual interest. In the accompanying diagram (Fig. 8), heavy lines imply strong interdependence, and dotted lines suggest alternative classifications. Thus, physics is represented as more dependent upon mathematics than is chemistry, while electrical and chemical engineering may be looked upon either as subdivisions of the general field of engineering or alternatively as branches of physics and chemistry, respectively. The biological sciences that are included are represented as being more closely related to chemistry than to physics. The status of medicine with respect to chemistry is represented in

TABLE 1.* Classification of Knowledge

<i>Philosophy</i>	<i>Science</i>	<i>History</i>	<i>Applied Sciences</i>
Principles			
Ontology (Reality)			
Epistemology			
	Philosophy of Science		
	Principles of Science	History of Science	
	<i>Abstract Sciences and General Methods</i>		
	Science of Order		
	Methodology		
	Logic		
	Mathematics		
	Metrology		
	Statistics,		
	etc.		Applied Metrology, Statistics, etc.
Philosophy of Nature	<i>Natural Sciences, General</i>	Natural History Evolution	
	<i>Physical Sciences</i>		Technology
	Physics		
	Mechanics, Dynamics		Applied Mechanics
	Matter, Energy, and Radiation		
	Special Physics		Physical Technology
	Chemistry		
	Physical and Theoretical		
	Mineralogy		Petrography
	Crystallography		
	Analytical and		Chemical Technology
	Special Chemistry		Metallurgy
	<i>Special Natural Sciences and</i>		
	<i>Descriptive Natural History</i>		
	Astronomy		
	Theoretical, Mechanical		Practical Astronomy
	Astrophysics		
	Geology		
	Physical and	Historical and	
	Theoretical	Stratigraphical	
	Geography, Physiography		Economic Geology
	Meteorology		Economic Geography

* Bliss, "The Organization of Knowledge." Henry Holt and Company, Inc., New York, 1920, pp. 302-330.
Reproduced by courtesy of the publisher.

TABLE 1. Classification of Knowledge (*Continued*)

<i>Philosophy</i>	<i>Science</i>	<i>History</i>	<i>Applied Sciences</i>
	<i>Biological Sciences</i>		
Philosophy of Life	Biology		
	Cytology, Ontogeny, and Embryology		
	Physiology and Ecology		Bio-geography
	Morphology		
	Genetics Paleontology		
	Phylogeny, Organic Evolution		
	Botany		Economic Botany
	Zoölogy		Economic Zoölogy
	<i>Anthropological Sciences</i>		
Philosophy of Human Life	History of Mankind		Hygiene
	Anthropology		
	<i>Psychological Sciences</i>		
	Psychology		Medical Science
	General and Comparative Individual		Applied Psychology
	Anthropological and Racial Social		Psychiatry
	<i>Social Sciences</i>		
	Sociology	Social-political History	Education
			Applied Social Science
	Ethnology	Ethnography	
	Folk-lore	Archeology	
Philosophy of Religion	Religion	History of Religions, Churches, Cults	Church-work, Missions Ministry, etc.
	Mythology		
Theology			
Ethics	Ethics (science of morals)		Applied Ethics, Philanthropy
			Government and Administration
Political Philosophy	Political Science		Practical Politics
Philosophy of Law	Jurisprudence		Law, Practice, etc.
	Comparative Law		
	Economics	Economic History	Industrial Economics, Commerce, Finance, Business, etc.
			Private Economy
Aesthetics, Philosophy of Art			Technology of Arts
			Technic of Fine Arts
	Philology		Grammar, Rhetoric, Oratory, and Criticism
	Linguistics	History of Languages and of Literatures	Dramatics

an indirect fashion, because chemistry is largely applied in medicine through intermediate studies having to do with the role of chemistry in biological processes broadly. A particular effort has been made to emphasize that physics and chemistry have a common meeting ground.

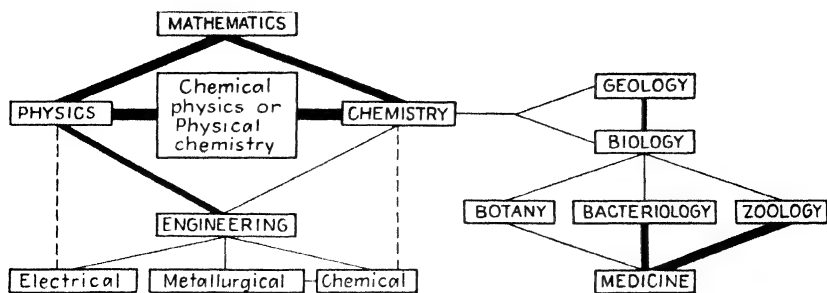


Figure 8. Interrelationships of the physical and biological sciences.

The very use of the terms chemical physics and physical chemistry suggests that there are realms of scientific knowledge in which the two fields are indistinguishable; and this is most certainly true. In the chapters that follow, the discerning reader will detect frequently the extent to which new information in physics has led to progress in chemistry. The reverse is equally true.

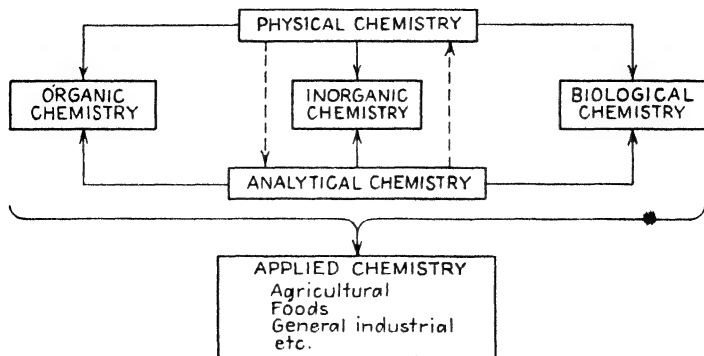


Figure 9. The fields of chemistry.

The Subdivisions of Chemistry. Again based more upon convenience than any real lines of demarkation, it is conventional practice to subdivide the science of chemistry into a number of reasonably distinct but nevertheless closely related fields. Figure 9 represents an effort to portray the relationship between them.

The fundamental and exacting laws of chemistry, the underlying principles, the theories, and the like, are generally considered to fall within the domain of *Physical Chemistry*. This kind of knowledge provides the basis for three of the other four subdivisions. *Inorganic Chemistry* is concerned largely with the inanimate objects of the physical universe, whereas *Organic Chemistry* is characterized by a more limited scope of interests that are closely allied (but by no means restricted) to living matter or the products of vital processes. Accordingly, *Biological Chemistry* is closely related to organic chemistry and provides the connecting link between chemistry and the biological sciences. To a considerable degree, *Analytical Chemistry* is a service area that is based in part upon physical chemistry and that provides methods of analysis used widely in all other phases of the chemical sciences.

The foregoing major subdivisions provide the basis and background for the evolution of all of the applied aspects of the science, including of course, chemical engineering. Only a few of the many applied fields are listed in Fig. 9. Some of these will be portrayed in considerable detail in the later portions of this book, and the major subdivisions also will be defined in more precise terms as the need arises.

The Impact of Chemistry upon Other Fields of Study. Those whose interests lie in non-technical areas or in sciences other than chemistry often are prone to question the wisdom of their investing the time necessary for the acquisition of a knowledge of chemistry. While it is certainly true that any individual's need for chemical information may be quite limited—depending upon his interests—the need nevertheless exists. The implications of chemistry in other realms of learning are so prevalent that chemistry is commonly looked upon as primarily a service subject. It is self-evident that the inclusion of courses in chemistry in practically all college curricula was not at the behest of teachers of chemistry. These requirements arose simply because experience demonstrated a need.

Perhaps a single illustration will serve to focus attention upon the point that a given incident in scientific progress may have striking repercussions in many other *apparently* unrelated fields of human activity. In the past few years the utilization of atomic energy for military purposes became a reality in the so-called "atomic bomb," and much progress has been made in the direction of non-military applica-

tions. This development was primarily the result of joint efforts of chemists, physicists, and engineers, and no one would question the statement that many new and significant problems have consequently arisen in these fields. Atomic energy per se together with the by-products of its utilization will in all probability exert secondary influences that may obscure in some measure the primary impact upon the physical sciences.

Progress in all of the biological sciences already has been and will continue to be markedly accelerated because of the developments referred to above. New tools and methods have been made available to the biologist. He now has at his command new and improved techniques for the study of plant and animal metabolism, factors involved in reproduction, growth, and a host of others. It is not too much to hope that the way may now be open to a complete understanding of one of the oldest riddles of science—the nature of the process of photosynthesis. In agriculture, it now becomes possible to study more objectively the manner in which fertilizers influence plant growth, the control of the diseases of plant life, etc. The field of medicine inherits new and improved methods for diagnosis, and really for the first time an exacting means for determining what happens to drugs that are administered in the treatment of disease and by what means their purpose is accomplished. New problems in medicine arise also because of the need for protection of personnel and populations against potentially harmful radiation and toxic substances used in connection with the utilization of atomic energy.

The effects upon the less technical fields are no less important. In government and law, problems of national and international regulation and control must be solved. New impetus has been given to the ideal of world government. More specifically, problems relating to the control of raw materials and the disposal of harmful waste materials have to be faced. These and other factors provide a changing scene that will influence the field of economics also for years to come. The successful utilization of atomic energy for domestic and industrial purposes will ultimately influence essentially every phase of our economy and will be felt particularly by the electrical, petroleum, gas, coal, and other solid-fuels industries. Insurance companies will face new and different elements of risk to both personnel and property. Sociologists must become concerned with redistribution of populations, philosophers need

consider new problems in morals and ethics, etc. In a degree never before fully realized, journalism is obligated to provide widespread, accurate, and understandable public information of a rather highly technical character.

These and many analogous factors arise to complicate life in present-day society merely because a few scientists were curious enough to pry into the secrets of nature. This is the essence of progress; it has happened repeatedly through the ages, and it will happen again and again.

Certainly these few illustrations will serve to show that all phases of human activity are susceptible to change resulting from scientific progress. It is assumed that those who must solve most of these attendant non-technical problems are not expected to become skilled physical scientists. They must depend upon the physicist and the chemist for the requisite technical information, but at the same time they must acquire a scientific background sufficient to permit them to understand and appreciate the significance of the information provided for them.

Chemistry and Current Events. The utility of a knowledge of chemistry is by no means restricted to those who will be involved in serious studies in the various areas of scholarly accomplishment. Practically every object with which we come into contact or use from day to day is either a product of chemistry or involves chemical processes in one way or another. The extent to which chemistry has a bearing upon our daily lives has in recent years become so great that technical topics are items of ordinary polite conversation, our vocabularies continue to accumulate technical terminology, and common articles of commerce are proudly proclaimed to represent the latest scientific advances. One can almost justify a knowledge of chemistry on the grounds that it enables one to detect pseudo-scientific claims that have become so much a part of the more fallacious and flatulent advertising with which we are bombarded.

It is becoming increasingly evident that a knowledge of chemistry is a useful possession of any intelligent member of society. One must in these times know something of science even to read newspapers and magazines intelligently and with full understanding.

Chemical products almost without end could be listed here as illustrations of common articles with which many are passingly familiar

but few understand or appreciate fully. A few typical items are dyes, synthetic rubbers, fibers such as nylon, synthetic gems, plastics, paints, antifreeze mixtures for automobile radiators, refrigerants, insecticides, drugs and medicines, etc.

Knowledge thus useful would appear to be worth the effort necessary for its acquisition. One may not, however, acquire a knowledge of chemistry by dealing in vague generalities, personal opinions, or random observations either in or outside of the laboratory. Chemistry must be studied in terms of concrete facts, expressed in the language of numbers, and rigorously supported by experimental evidence. For limited purposes, however, it is believed that this may be accomplished without becoming too involved in training of the type that is suitable for those who would elect careers in scientific investigation.

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Matter and Energy

IF IT WERE possible to enumerate all of the outwardly different kinds of material objects in the world about us, the result would be a number so large that it would be almost meaningless. Because the science of chemistry is in some measure concerned with all of these objects, it becomes necessary to inquire whether things having externally distinguishing attributes may not in fact possess many characteristics in common. Since the answer to this question is an affirmative one, the great host of common objects that must be studied may be classified at once in terms of their similarities and their study is correspondingly simplified. Chemistry, like any other subject of study, requires organization and systematization; orderliness is more than a virtue—it is an absolute necessity.

Terminology. Before proceeding with some of the simpler problems of classification, attention must be called to a few common terms and the sense in which they are applied in chemistry. *Matter* is defined as anything that has mass or occupies space and is capable of undergoing change. There are many different kinds of matter, and yet one may find, from a wide variety of sources, samples that appear to be and are alike in all respects. The term *substance* is applied to any material all parts of which and all specimens of which are alike in every way. The use of the term substance should imply purity or uniformity; unfortunately the common usage is not so restrictive.

Each substance is identifiable in terms of certain visible or measurable characteristics that set it apart from all other substances. One may distinguish an oak tree from a birch by characteristics such as the color and texture of the bark, the shape of the leaves, etc. Similarly, sulfur may be identified by its color, odor, behavior upon being heated, etc. The characteristics through which substances may be identified are called *properties*.

It is common knowledge that matter may exist in many different

conditions and yet all of these may be classified quite simply in terms of no more than three categories. Everyone has observed that solid ice melts to form liquid water, which in turn is changed—upon application of heat—to steam (gaseous water, or “water vapor”). Regardless of the physical *form* in which water exists, it is still water so far as its chemical nature is concerned. Not every substance is capable of existing in as many as three different forms, but every object known can exist in one or more of the three. We may at once conclude that at least a gross simplification of a complex problem may be had merely by classifying all material objects as *solids*, *liquids*, or *gases*. These are the so-called “three states of matter,” and their individual characteristics will be discussed later.

Energy is defined as the ability to perform work and is that which either causes changes to occur or results from them. Heat, light, and electricity are manifestations of energy with which the student is already familiar, and others will be encountered as the study of the subject progresses.

In the examples given above, each of the changes in the form of water from solid to liquid to gas required that energy be *supplied*. When ice is heated, it melts; when water is heated, it boils. It is important also to recognize that these changes are *reversible*; *i.e.*, if water vapor is cooled (energy withdrawn), it is changed to liquid water. If liquid water is cooled, it solidifies. Consequently, it may be concluded that some changes which require that energy be supplied may be reversed by a withdrawal of energy.

Much emphasis has been placed thus far upon the occurrence of changes of one sort or another. It has been indicated also that water may be converted from one physical state to another without being altered with respect to its chemical make-up or composition. Any transformation that occurs without alteration in the chemical composition of the substances involved (and consequently concerned only with energy) is called a *physical change*.

Up to this point we have introduced only a few of the terms that are a part of the language of chemistry. The task of acquiring new vocabulary is a continuing one. Increasing breadth of knowledge of chemistry is reflected in an ever-increasing expansion of the terminology required, and in this respect the study of chemistry is quite like the study of any other subject.

Chemical Composition. Although it is important to know that water may undergo physical change upon application or withdrawal of heat energy, it must not be inferred that other forms of energy will necessarily result in the occurrence of the same kinds of changes. If, for example, water is subjected under suitable conditions to the action of electrical energy, the water is changed from the familiar liquid to the two quite different colorless gases, hydrogen and oxygen. It seems fair to conclude that the classification of matter according to the physical state in which it exists is convenient and yet provides no information whatever concerning the detailed make-up of the substances so classified. This conclusion should not be cause for surprise. After all, water and castor oil are both colorless liquids, and yet their taste and physiological action alone are sufficient to emphasize that they must differ in other respects. The gaseous air that we breathe and the gas that we burn as a fuel have many properties in common, and yet efforts to substitute one for the other do not meet with any marked degree of success. We must therefore seek a basis of classification which is based upon a more complete understanding of the nature of the things of which different forms of matter are made.

It has been stated that water may be broken down by means of electrical energy to form hydrogen and oxygen. These two substances must be less complex than the water from which they were obtained. Similarly, it may be shown that natural gas consists primarily of a substance that can be broken down (*decomposed*) into two simpler substances, hydrogen and carbon. "Dry ice" is a substance that upon decomposition is found to be made of carbon and oxygen. We may now decide that hydrogen, oxygen, and carbon are substances simpler in their make-up than the substances from which they were obtained, and we may proceed by experiment to determine whether hydrogen, or oxygen, or carbon may be decomposed into still simpler forms of matter.

Elements. Substances such as hydrogen, oxygen, carbon, and other familiar substances including sulfur, iron, mercury, nitrogen, lead, etc., are known as elements and may be looked upon as the building stones of which more complex forms of matter are composed.

The idea that all of the many complex forms of matter in the world are made up of a relatively few simple substances is not new. The Greek philosopher Democritus (*ca.* 460?–362? B.C.) was probably one of the earliest proponents of the view that all matter is corpuscular,

that it consists of simple discrete particles. He attempted to explain the composition of matter and the changes that it undergoes in terms of particles that were believed incapable of further subdivision. These fragmentary concepts persisted through the centuries, but progress came only slowly. As recently as the latter part of the eighteenth century, Lavoisier published a table of elements ("Tableau des substances simples") that included not only some of the more common elements but more complex bodies (which up to that time had not been decomposed) and heat and light as well. From this fact it is apparent that, although the basic idea was sound, its full development required the accumulation of much additional information, and it was not until early in the nineteenth century that the next great step forward was to be made.

It may have been noticed that the term element has not yet been defined precisely. The reason is that the traditional definition is inadequate in the light of present-day knowledge and accordingly has to be "hedged." We shall

therefore not attempt here to define the word in exacting terms but shall proceed on the basis of the provisional view that elements are relatively simple forms of matter from which more complex forms may be made. After the necessary additional facts have been presented, the term will be defined in wholly unambiguous language.

Since the composition of all forms of matter may be represented in terms of the constituent elements, the number and relative abundance of these simple substances become of particular interest. At the present time, ninety-six elements are known. Only a few of these are at all common and abundant in nature, while certain others are not found in nature at all; they are produced only in the laboratory. The relative abundance of some of the elements in the earth's "crust" (including terrestrial waters and the atmosphere) is shown schematically in Fig. 10. From this it is apparent that about one-half of all matter con-

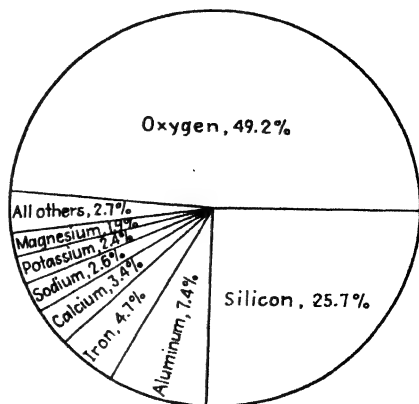


Figure 10. Relative abundance of the elements.

sists of the element oxygen, while eight elements make up a total of over 97 per cent. The remainder includes many common and useful elements, *e.g.*, hydrogen, sulfur, chromium, carbon, nickel, copper, mercury, zinc, lead, tin, gold, silver, platinum, etc. Some elements stand very low on the scale of relative abundance, and yet because their natural occurrence is localized, they are readily available.

Compounds. Three illustrations of the production of elements by the decomposition of more complex forms of matter have been used; these may be summarized as follows:

Water decomposes into hydrogen and oxygen.

Methane
(natural gas) } decomposes into hydrogen and carbon.

Carbon dioxide
(dry ice) } decomposes into carbon and oxygen.

Because carbon, hydrogen, and oxygen are recognized as relatively simple forms of matter, it follows that water, methane, and carbon dioxide represent more complex forms which may not be classed as elements. Obviously, what is needed is a term which expresses the idea that these substances bespeak a degree of complexity greater than do the elements. The adjective *compound* means literally "composed of two or more ingredients." We may then use the same word as a noun and specify that a chemical compound is a substance composed of two or more elements, and it is at once apparent that this term is satisfactory so far as the three cases cited above are concerned. It should be recognized further that compounds have their own characteristic properties. Dry ice is a white crystalline solid, whereas the elements from which dry ice is formed are a black solid and a colorless gas. When black solid carbon and colorless oxygen gas combine to form dry ice, the properties that characterize the two elements disappear and the product of the chemical union has properties that are very different from those of the component elements. Although there are exceptions, this illustration is typical.

Still another characteristic of chemical compounds needs to be recognized. With respect to the compound called methane, for example, we may admit that it is composed of carbon and hydrogen and still

leave unanswered the question, "how much carbon, and how much hydrogen?" It would be indeed unfortunate and no end confusing if methane turned out to be an undependable chemical individual that sometimes contained more carbon than hydrogen and at other times just the reverse. Such is not the case. That the composition of a pure chemical compound of natural origin is absolutely constant is as sure as death and surer than either taxes or final examinations. Carbon and hydrogen unite to form methane in a perfectly definite way such that this pure compound contains 74.87 per cent carbon and 25.13 per cent hydrogen. That is, to produce 100 lb. of methane, one would have to combine 74.87 lb. of carbon with 25.13 lb. of hydrogen. On the other hand, we should not place undue faith in the simplicity of the habits of nature. True, the composition of any individual compound is constant, but might not carbon and hydrogen unite in some other weight ratio to form some compound other than methane? As a matter of fact, these two elements combine in many different ways to form many different compounds, but each of these has its own definite composition and characteristic properties. In summary, it may be said that the composition of a pure chemical compound is fixed and definite. This is in effect a statement of the law of constant composition, which is also known as the law of definite proportions.¹

Compounds may be, but need not be, formed directly from elements. For example, assume that two elements A and B unite to form a compound AB and that X and Y unite to form another compound XY . These two compounds may then combine to form a still more complex compound $ABXY$. This, in turn, might change in a manner such as to produce element A and a compound BXY , or element X and a compound ABY , etc. In addition, numerous other approaches to compound formation will be encountered.

The foregoing cases serve also as illustrations of chemical changes, or—as they are more commonly called—*chemical reactions*. A chemical change may involve union of two or more substances or the decomposition of one or more; in any case, substances with different properties are formed. Chemical and physical changes differ in that one involves changes in chemical composition while the other does not. The two

¹ For the present, the student should interpret the use of the term *law* simply as a statement of fact. In Chapter 7, the status of this term as it is used in science broadly will be considered in some detail.

kinds of change have one characteristic in common: both involve changes in energy.

Mixtures. Quite unlike compounds, mixtures are not of definite composition. The elements gold and silver may be brought together (without the occurrence of a chemical reaction) in any desired proportions by weight; the mixture may have whatever composition happens to be wanted. Similarly, one may mix one pound of table salt and ten pounds of cane sugar; or five pounds of each; or one pound of one and a hundred of the other, etc. In any event, *the individual components of a mixture retain their characteristic properties*, and in this respect, also, mixtures differ from compounds. The third way in which compounds and mixtures differ is concerned with the manner in which they may be resolved into their component parts. In order to separate a compound into its components, it is necessary to bring about a chemical change, *e.g.*, the decomposition of water into hydrogen and oxygen. Mixtures, on the other hand, may be separated into their components by purely mechanical means and therefore without the occurrence of any change in chemical composition. For example, a mixture of lead shot and powdered sulfur may be separated, because the sulfur will float on the surface of water and the lead shot will sink to the bottom. Similarly an intimate mixture of particles of sand and ice may be separated by allowing the ice to melt (a physical change) and pouring off the resulting liquid water (a purely mechanical operation). The chemical composition of the water and the sand is not changed in either of these processes.

The frequency with which it will be necessary to refer to mixtures makes it desirable here to introduce two additional descriptive terms, *i.e.*, homogeneous and heterogeneous. If the component parts are separately distinguishable by the unaided eye, the mixture is said to be *heterogeneous*. A mixture of salt and black pepper is certainly heterogeneous, because the individual particles of each are readily visible. If one should grind such a mixture until the particle size is reduced sufficiently, the mixture has a uniform gray appearance and one can no longer detect visually the individual particles. A mixture that to the unaided eye appears to be uniform in composition is said to be *homogeneous*. A mixture of water and alcohol is homogeneous; one cannot distinguish the one from the other by visual means. This criterion of

visual detection is indeed a crude one, but satisfactory for present purposes.

Matter and Energy. It has been pointed out that matter may exist in different physical states (solids, liquids, gases, or mixtures thereof) and that the three states of matter are mutually interconvertible through the agency of suitable energy changes. Matter may also exist in different conditions of chemical composition, and chemical changes are always accompanied by characteristic energy changes. All of this bespeaks a very close relationship between matter and energy.

In 1906, Albert Einstein formulated a relationship that is of such far-reaching importance that it merits more detailed consideration than is warranted here. He proposed that matter and energy are convertible one to the other and related by the mathematical expression

$$E = mc^2$$

where E and m represent energy and mass (matter), respectively, and c is the velocity of light. This concept is the fundamental basis for the accomplishment of utilization of atomic energy (as will be shown later), and it is of interest to note by way of contrast that these two milestones in the progress of science were separated by a period of only about forty years. In the utilization of atomic energy, relatively large masses are converted into energy; in ordinary chemical reactions the accompanying energy changes correspond to only negligibly small changes in mass.

It may be concluded that appropriate energy changes may result in either chemical or physical changes in matter and that matter may be converted to energy, and vice versa. Similarly, one form of energy may be converted to one or more other forms of energy. All of these things may happen without any change in the sum total of matter and energy involved. These facts collectively constitute the *law of conservation of mass-energy*, which may be stated as follows: All changes involve transformations in the form of matter and energy but no net change in the sum total of the two.

The Atomic Theory. Classification of matter in terms of elements and compounds is at the same time both useful and unsatisfactory. That compounds are made up of elements suggests that, contrary to

views that prevailed for a long time, the elements may be composed of still simpler forms of matter. The quest for an understanding of the nature of matter and a detailed knowledge of the character of the ultimate particles of which all matter is composed has persisted throughout the history of science. The search continues.

Attention has already been called to the fact that the concept of



Figure 11. John Dalton. (Courtesy of the Franklin Institute of Philadelphia, Pa.)

fundamental “particles” of matter was common among the early Greek philosophers and indeed probably antedated them. These ideas persisted without any major step forward until the period from 1800 to 1810. Within that period, the English chemist John Dalton (Fig. 11) evolved a set of ideas that were destined to be the forerunner of a whole series of notable achievements.

John Dalton was a teacher and scientist of broad interests. Although he was more inclined toward abstract speculation than toward concrete experiments, he concerned himself with a wide variety of natural phenomena. He made the first systematic study of color blindness (a condition with which he was afflicted) and through his lifetime accumulated voluminous data on meteorology. These latter studies aroused his

interest in the nature and behavior of the gases that make up the atmosphere and led indirectly to his major contribution to an understanding of the nature of matter. Dalton believed that the chemical elements such as nitrogen and oxygen are made up of *atoms*, and he was chiefly concerned with trying to understand how the atoms of the various elements behave when these elements unite to form compounds. He attempted to portray differences in the constitution of different kinds of atoms by means of diagrams such as those shown in Fig. 12 and thereby to account for their properties.

There would be little reason other than purely historical interest to reproduce here the conclusions that Dalton reached. It is a simple fact that most of his ideas later proved to be either partially or wholly erroneous. This fact should not be surprising, for it certainly is not unusual. Very few sets of ideas, which we call *theories*, withstand the test of time in the form existing at their inception. Dalton's views have to be evaluated in relation to the state of advancement of knowledge at the time and in terms of their influence upon subsequent developments. The atomic theory as it is usually presented today would be neither recognizable nor understandable to John Dalton; but because of the extent to which his work influenced its development through the years, it is still known as Dalton's atomic theory.

Stripped of all its original ambiguities and revised in the light of developments since Dalton's time, the essential aspects of the atomic theory of the constitution of matter may be enumerated and illustrated in very simple terms, as follows:

1. The chemical elements, of which all forms of matter are composed, are not themselves indivisible but consist of tiny invisible particles called atoms.

2. The atoms of different elements are different with respect to size, weight, and their physical and chemical properties in general. Accordingly, one would expect that an atom of the element iron might be very different from an atom of the element sulfur, and yet this would not preclude the possibility that atoms of different elements might be similar in at least some respects.

3. Atoms of the same kind or of different kinds unite to form *molecules*. If the atoms are of the same kind, this union results in molecules of an element; if the atoms are unlike, the result is molecules of a compound. For example, if two atoms of hydrogen unite, they form a

molecule of the element hydrogen. If atoms of hydrogen and oxygen combine, they form molecules of the compound called water. The

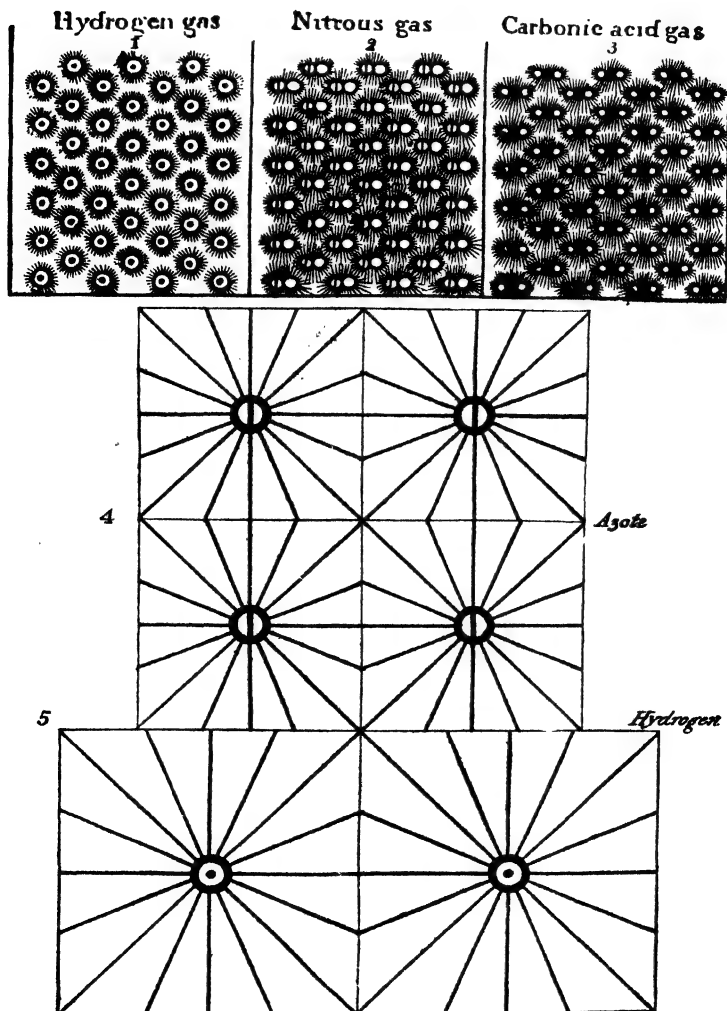


Figure 12. Some of Dalton's pictures of atoms. (Reproduced from "A History of Chemistry," by F. J. Moore, Copyright, 1931, by William T. Hall.)

important point is that the atoms are the participants in all kinds of chemical changes whether they be changes involving the formation or the decomposition of the more complex forms of matter.

4. When atoms unite to form molecules, they do so only in simple whole-number ratios. Thus, two atoms of one kind may unite with one of another kind; three of one kind and two of another; one of one kind and five of another; etc. In the formation of water, for example, two atoms of hydrogen unite with one atom of oxygen to form a molecule of water.

5. Atoms of the elements may unite in different ratios to form different kinds of molecules. Thus it is not necessary that hydrogen and oxygen must always combine in a two-to-one ratio to form molecules of water. Under appropriate conditions, these elements may combine in a one-to-one atomic ratio to form molecules of the compound known as hydrogen peroxide.

It requires no great knowledge of chemistry to recognize that the ideas embodied in the atomic theory are ones of far-reaching implications. With reference to Dalton's position with respect to these ideas we shall forego the temptation to apply to him (as is commonly done) the much overworked designation "the father of modern chemistry." (One history of chemistry lists no less than six fathers.)

Recognition of the atom as a particle more fundamental in character than either compounds or elements leads logically to the question: may not atoms be composed of still smaller particles? This kind of inquiry goes on and on with the objective of finding eventually the truly fundamental particles in terms of which the composition of matter may be fully understood.

The Measurement of Mass and Energy. Both chemical and physical changes may be understood rigorously only in terms of the *quantities* of matter that undergo transformation. It is therefore consequential to have as nearly as possible a uniform and standard basis in terms of which to express weight, volume, distance, and the like. Unfortunately, the ideal degree of uniformity has not been achieved; practices differ not only between but also within countries. Anyone who has traveled in Mexico, for example, may have experienced annoyance at highway markers that specify distances not in miles but in kilometers, unless, of course, one chanced to know that one kilometer is approximately five-eighths of a mile (or, more exactly, 0.6214 mile). Because a full discussion of some of these problems seems premature, only two units will be introduced here. Others will be cited when the need for them arises, and a more complete compilation is included in the Appendix.

The unit of mass that is most commonly used in scientific work is the *gram* (abbreviated g.). This unit is a part of the metric system, which was adopted by law in the United States in 1866. Some idea of the quantity of matter represented by one gram follows from its relation to the familiar domestic unit, the pound; one pound is equivalent to 453.59 grams. Perhaps helpful also is the fact that three common domestic coins have the following average weights in grams: 10¢ coin (2.5 g.), 25¢ coin (6.25 g.), 50¢ coin (12.5 g.). Throughout the remainder of this book, weights will be expressed in various units, but most commonly in terms of grams.

Quantities of heat energy are expressed in terms of a unit called the *calorie* (abbreviated cal.). By definition, a calorie is the quantity of heat required to raise the temperature of one gram of water to the extent of one degree on the centigrade temperature scale.¹ This is the so-called *small calorie* which is so commonly used in dietetics to express the energy value ("calorific value") of foods. Also used extensively is a unit one thousand times as large, the *large calorie* (abbreviated Cal.). Unless otherwise specified, the small calorie will be used in the pages that follow.

EXERCISES

The exercises listed below, and those at the end of each of the remaining chapters, are designed to provide the student with a basis for study. Each set of exercises will include a list of new terms, laws, principles, etc., and it is anticipated that the student will be prepared to state the laws and give carefully worded definitions of terms. In addition, each set of exercises will include questions and problems that will focus the student's attention upon the more important points covered in each chapter and will provide an indication of the extent to which the student will be expected to use new information as it is acquired.

1. *New terms:* energy, compound, caloric, substance, atom, homogeneous, matter, properties, physical change, molecule, gram, chemical change, heterogeneous.
2. *Laws:* the law of constant composition, the law of conservation of mass-energy.
3. Outline the chief ideas embodied in the atomic theory.

¹ For an explanation of this temperature scale, see Chapter 8.

4. Cite three ways in which compounds differ from elements.
5. What are the "three states of matter"?
6. In what respects are chemical and physical changes similar?
7. From everyday experience, give examples of reversible physical changes.
8. What is the general nature of the type of change commonly described as *decomposition*?
9. What three elements are the most abundant? Give the approximate percentage represented by each.
10. What is meant when one refers to the "chemical composition" of any form of matter?
11. Two samples of a compound are found to contain different percentages of carbon, hydrogen, and oxygen. What conclusion may be drawn from this information?
12. Cite three ways in which mixtures differ from compounds.
13. How is matter classified according to its chemical composition?

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Chemical Notation

THE WIDESPREAD application of all sorts of symbols is ample testimony for the convenience of these abbreviated modes of expression. Probably

the ampersand, &, is the single most widely used symbol; others so common that they will be recognized at once are R, ©, \$, π , c/o, A, etc. Pharmacy, business and finance, music, the building trades, mathematics, woodcraft, and chemistry are only a few of the widely different fields of activity that have their own peculiar symbolisms. In every

case, the object is to impart information briefly and concisely through an association in thought. The extent to which symbolism simplifies the exchange of information in the field of chemistry cannot well be described; one must come to appreciate its convenience through actual use.

Names and Symbols for the Elements. The forerunners of the symbols that are now used to represent the chemical elements were the crude characters inscribed in the writings of the alchemists. In alchemical manuscripts, a given symbol commonly had different connotations; similarly, several different symbols were used to denote a single material. A few typical examples of alchemical symbols are shown in Fig. 13.

Early in the nineteenth century our modern system of chemical symbols was invented by the Swedish chemist Jöns Jakob Berzelius (Fig. 14). With suitable modification and extension the system of

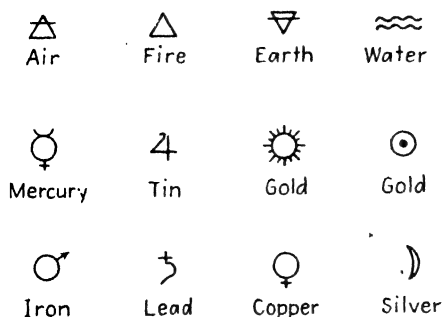


Figure 13. Some symbols used by the alchemists.

Berzelius is essentially that in use today. Symbols for the elements are derived from the corresponding names in a manner that is described below. First, however, it should be recognized that the *names* of the chemical elements have not been assigned on any systematic basis. It is a tradition in chemical science that the discoverer of a new element is privileged to assign whatever he considers to be a suitable name (and symbol). Consequently, a wide variety of motives have dictated the selection of names. For example, numerous discoverers of elements have wished to honor their native countries, and this is reflected in names such as francium, germanium, europium, etc. The names of some elements have been selected to perpetuate the names of famous scientists; the names of still other elements have their basis in some specific or unusual properties of those elements.

For fourteen of the ninety-six known elements, the symbols are simply the initial (capital) letters of the English or Latin names of those elements. Of the fourteen, the student will have need early to know only seven, the names and symbols of which are:

Carbon C	Nitrogen N	Sulfur S
Iodine I	Oxygen O	Uranium U
	Phosphorus P	



Figure 14. Jöns Jakob Berzelius. (Courtesy of the Edgar F. Smith Memorial Collection, University of Pennsylvania.)

For all of the remaining eighty-two elements, the symbols employ the initial (capitalized) letter and one other letter (*not* capitalized) from the English or Latin names of the elements. Of these eighty-two, the student's working vocabulary at the outset need include only eleven.

Bromine	Br	Iron (<i>ferrum</i>)	Fe	Silicon	Si
Calcium	Ca	Lead (<i>plumbum</i>)	Pb	Silver (<i>argentum</i>)	Ag
Chlorine	Cl	Nickel	Ni	Tin (<i>stannum</i>)	Sn
Copper (<i>cuprum</i>)	Cu			Zinc	Zn

Symbols for other elements will be introduced as the need for their use arises; a complete list is given in the Appendix.

The Interpretation of Symbols. The symbols for the elements are more than mere abbreviations. In addition to denoting a particular chemical element, each symbol stands for a definite quantity of that element. Since we know that elements are made up of atoms, at first thought it might appear desirable to have the symbol for an element represent *one atom* of that element. However, the weight of any kind of atom is so small that the number representing that weight would be meaningless; the human mind cannot associate real significance with so small a quantity. One must conclude that it would be preferable to have each symbol stand for a large and definite number of atoms, so that the corresponding weight will be a number that will carry real meaning.

Chemists have solved this problem by adopting a system of *relative weights*. That is, one element is selected as a standard, and a number is assigned to represent the weight of the atom of that particular kind of element. Because oxygen is the most abundant element and because it forms compounds with most of the other elements, oxygen is used as the standard. In order that the *relative weights* of all other kinds of atoms will be represented by numbers greater than unity, the oxygen atom is assigned a value of 16.0000 weight units. Now it should be understood clearly that this does not represent the true (absolute) weight of an individual oxygen atom. Exactly 16.0000 *grams* of oxygen, for example, represents a very large number of oxygen atoms. By means that need not be considered here, it is known that this number is 602,000,000,000,000,000,000,000. This is known as Avogadro's number, in honor of the Italian scientist Amadeo Avogadro (Fig. 15), and is more conveniently expressed in exponential form, 6.02×10^{23} (which simply means the number 6.02 multiplied 23 times by the number 10). This is certainly a large number, but it is necessary that the number be large if the corresponding weight is to be large enough for convenient usage. The weight of 6.02×10^{23} atoms of *any* element is called the

atomic weight of that element. Chemists and physicists have devised both direct and indirect methods for the very accurate measurement of the atomic weights of the elements; a table included in the Appendix gives a complete list of the most accurate known values.

It will be seen, for example, that the atomic weight of hydrogen (the lightest of all the elements) is 1.0080. This means that if we had a sample of pure hydrogen containing 6.02×10^{23} hydrogen atoms and were to weigh this sample as accurately as possible, we should find the weight to be 1.0080 grams. Similarly, 6.02×10^{23} atoms of oxygen are found to weigh 16.0000 grams, from which it follows that an oxygen atom must be approximately 16 times as heavy as a hydrogen atom. Further, the atomic weight of sulfur is 32.066; hence the sulfur atom is about twice as heavy as the oxygen atom and about thirty-two times as heavy as the hydrogen atom.

Accordingly, each symbol should be interpreted as representing (1) a particular chemical element, (2) a specific number of atoms of that element, and (3) a definite weight of that element, *i.e.*, one atomic weight. When, as is usually true, atomic weights are expressed in grams, they are called *gram-atomic weights*, or *gram-atoms*. Because these weights are relative rather than absolute, they may be expressed in any desired units, such as grams, pounds, tons, etc.

It is reasonable to inquire whether one ever needs to know the absolute weight of any single atom. Such information is sometimes required and may be had simply by dividing the atomic weight of the element in question by 6.02×10^{23} . For the purposes of this book, the student need not memorize any atomic-weight values; this information will be given wherever needed, or it may be had by reference to the Appendix.

Formulas. Since elements combine to form more complex kinds of



Figure 15. Amadeo Avogadro. (Courtesy of the Edgar F. Smith Memorial Collection, University of Pennsylvania.)

matter, it seems logical to represent the composition of the latter in terms of the appropriate symbols. As indicated previously, the elements hydrogen and oxygen combine in the ratio of two atoms of hydrogen to one of oxygen to form *molecules* of the compound known as water. The *formula* for this particular compound is written H_2O ; the subscript 2 shows that the water molecule contains two atoms of hydrogen. Actually, one might properly write the formula H_2O_1 , but subscripts of unity are always omitted.

From this simple illustration it is seen that formulas are convenient collections of symbols that represent the composition of molecules. We must now recall that the symbols that make up formulas have significance in terms of numbers of atoms and weights. The formula H_2O implies that $2 \times (6.02 \times 10^{23})$ atoms of hydrogen have combined with 6.02×10^{23} atoms of oxygen; and because each molecule of water contains two atoms of hydrogen and one of oxygen, it follows that the number of molecules of water represented by the formula H_2O must be 6.02×10^{23} . We may thence proceed to the question, what is the relative weight of the water molecule? This question may be answered readily because we already know the relative weights of the atoms that make up this kind of molecule. The relative weight of the water molecule is twice the relative weight of the hydrogen atom (2×1.0080) plus the relative weight of the oxygen atom (16.0000),

$$(2 \times 1.0080) + 16.0000 = 18.0160$$

This number, 18.0160, the relative weight of the water molecule is called the *molecular weight* of water or, when expressed in grams, is called the gram-molecular weight.

In summary, the formula H_2O shows the identity of the elements that make up the compound and the number of atoms (of each kind) per molecule and in addition denotes a definite number of molecules (6.02×10^{23}) having a relative weight equal to the sum of the relative weights of all of the constituent atoms.

Let us next consider a case in which like atoms combine to form molecules. A number of the common gaseous elements, including oxygen, hydrogen, and nitrogen, exist under ordinary atmospheric conditions in the form of molecules containing two atoms each. Consequently, the formulas for these gases must be written O_2 , H_2 , and N_2 , respectively. The formula O_2 , for example, implies that $2 \times (6.02 \times 10^{23})$

atoms of oxygen combine to form 6.02×10^{23} molecules of oxygen and that the molecular weight of oxygen is twice the atomic weight, that is, $2 \times 16.0000 = 32.0000$.

Still another example is a compound consisting of molecules that contain two atoms of hydrogen, one of sulfur, and four of oxygen. From this information alone one may write the formula H_2SO_4 . If, now, one wishes to know the molecular weight of this compound, it is necessary only to look up the appropriate atomic weights, that is, $\text{H} = 1.0080$, $\text{S} = 32.066$, $\text{O} = 16.0000$. Accordingly, the molecular weight of H_2SO_4 is $(2 \times 1.0080) + 32.066 + (4 \times 16.0000) = 98.082$. One gram-molecular weight of this compound (*or any compound*) contains 6.02×10^{23} molecules, and the absolute weight (in grams) of the individual molecule is equal to the gram-molecular weight divided by Avogadro's number.

The foregoing illustrations have been used without any consideration of how or why the respective atoms combine as they do. These problems require information that has not yet been presented. Meanwhile, formulas should be looked upon merely as convenient means for the representation of the *composition* of those chemical products formed by the union of atoms of the elements and should be interpreted as accurate specifications of the relative weights of the molecules involved. The examples that have been used may imply that one must know the composition of a compound in order to get a value for its molecular weight. Such is not the case. There are both chemical and physical methods by which we may measure molecular weights by experiment. These determinations together with a knowledge of the experimentally determined percentage composition of the compound permit the chemist to establish the correct formulas for compounds.

Attention may be called here to still another aspect of formula writing, namely, the order in which the symbols are written. For example, instead of H_2SO_4 , why not write $\text{O}_4\text{H}_2\text{S}$? Although other considerations are involved in some cases, the general rule is that in writing the formulas for compounds the symbol of the most metallic element is written first and the others in order of decreasing metallic character. Finally, it must be made clear that the subscripts in chemical formulas modify only the next preceding symbol. Thus, in the formula $\text{H}_4\text{P}_2\text{O}_7$, the subscript 4 refers only to H; the subscript 2 applies only to P; the 7 modifies only the symbol O.

The Percentage Composition of Compounds. A problem that commonly arises is that of calculating the percentage of some one or more elements in a particular compound. This may be illustrated as follows: Ordinary sea sand consists largely of a compound of silicon and oxygen combined in the ratio of one to two. Since silicon is more metallic than oxygen, the formula is written SiO_2 . Suppose, now, that one wished to know the percentage of silicon in this compound. Stated in other words, if we have 100 g. of the pure compound, how much of the sample is silicon?

From the atomic weights of silicon (28.06) and oxygen (16.00), it follows that the molecular weight is 60.06, whence

$$\begin{aligned}\% \text{ Si in SiO}_2 &= \frac{28.06}{60.06} \times 100 \\ &= 46.72\%\end{aligned}$$

The percentage of oxygen in this compound is, of course, the difference between 46.72 and 100 per cent, or 53.28 per cent. The same result is obtained by calculating the percentage of oxygen in the same way as indicated above, *i.e.*,

$$\begin{aligned}\% \text{ O in SiO}_2 &= \frac{32.00}{60.06} \times 100 \\ &= 53.28\%\end{aligned}$$

As another illustration, suppose that we were interested in ordinary limestone as a potential commercial source of the metal (element) calcium. For purposes of simplification, it will be assumed that the limestone consists of essentially *pure* calcium carbonate, which is a compound having the formula CaCO_3 . If we propose to produce calcium from this compound, it is rather obvious that it would be important to know how much calcium we could get from some given quantity of the compound, *i.e.*, we should wish to know the percentage of calcium in calcium carbonate. By looking up the atomic weights and adding the atomic weight of calcium (40.08), that of carbon (12.01), and three times the atomic weight of oxygen (3×16.00), it is found that the molecular weight of CaCO_3 is 100.09. It is seen by inspection that the compound is approximately 40 per cent Ca, but calculated as shown above,

$$\begin{aligned}\% \text{ Ca in CaCO}_3 &= \frac{40.08}{100.09} \times 100 \\ &= 40.04\%\end{aligned}$$

Similarly,

$$\begin{aligned}\% \text{ C in CaCO}_3 &= \frac{12.01}{100.09} \times 100 \\ &= 12.00\%\end{aligned}$$

and by difference $[100\% - (40.04\% + 12.00\%)]$ the percentage of oxygen in the compound is 47.96 per cent.

In these as in all other cases, if the formula of the compound and the atomic weights of the elements concerned are available, the percentage of any constituent or constituents may be calculated by operations involving nothing more than simple arithmetic.

Chemical Analysis. In Chapter 2, *analytical chemistry* was designated as one of the more or less definite subdivisions of the science of chemistry. Because some of the preceding discussion is concerned broadly with the problem of the exact composition of chemical substances, it is appropriate here to consider the manner in which analytical chemistry contributes to the sciences as a whole.

If, as suggested above, one were interested in a particular naturally occurring deposit of limestone as a potential source of calcium, it would be unlikely that the material would consist of pure CaCO_3 . Rather, it would contain principally CaCO_3 together with one or more of a wide variety of possible impurities. One of the first things to be done would be to secure a representative sample of the material and "have it analyzed." By this it is meant that one would seek the services of an analytical chemist and have him carry out such operations as may be necessary to determine exactly the chemical composition of the sample in question. In this manner it might be found that the material consists of 95 per cent CaCO_3 and 5 per cent impurities. One might then seek to determine (by known methods of analysis) the identity of the impurities present and the percentage of each.

Still another example is the case more related to a knowledge of chemical formulas. While it is true that percentage composition may be calculated from formulas, the latter are not always known. Chemists commonly produce in the laboratory new compounds of unknown formula and must necessarily face the problem of establishing the cor-

rect formulas. To do this one must know (or determine by experiment) the identity of each element present in the pure compound. Then, by chemical analysis the percentage composition of the compound must be determined. This information provides a basis for the establishment of chemical formulas. In some cases it is necessary to determine also by means of suitable experiments the molecular weight of the compound of unknown formula. There are several different ways in which this may be done, but these need not be discussed here. The point that it is desired to emphasize is that the establishment of correct chemical formulas has a sound basis in experiment and depends largely upon application of the methods of analytical chemistry.

The preceding remarks are not intended to imply any limitations upon the field of analytical chemistry or to illustrate adequately the scope of activities of the analytical chemist. In addition to the actual performance of chemical analyses as a service for others, the analytical chemist carries out many and varied studies designed to provide new and improved methods of analysis. The term chemical analysis has been defined as a *decomposition* effected for the purpose of determining the percentage composition of chemical substances. Actually, this definition is too restrictive. Perhaps it is better to designate chemical analysis as any operations (chemical or physical) performed in order to establish the composition of any form of matter.

The Description of Chemical Changes. The adoption of a set of symbols for the elements and their use in constructing formulas for compounds suggest that both symbols and formulas are suitable for use in the description of chemical reactions. One might go into the laboratory and bring together appropriate elements or compounds under conditions such that they can combine to form a more complex compound. (Such operations come under the heading of *synthesis*, a term that in chemistry implies the formation of a relatively complex form of matter from simpler substances.) One could, of course, describe all that was done by writing a detailed essay including all of the information necessary for someone else to repeat successfully the same experiment. This, however, would be so lacking in conciseness that it would be impractically inconvenient. A much more satisfactory alternative may be illustrated as follows; it is applicable to essentially all kinds of chemical reactions and is in no sense restricted to synthesis or to the operations of analytical chemistry.

Chemical Equations. In the course of certain experiments it is discovered that a compound of iron having the formula Fe_2O_3 enters into chemical change (*reacts*) with hydrogen, H_2 , *under specified experimental conditions* and that the products of this chemical change are metallic iron and steam. In the everyday language of chemistry one would state that "iron oxide reacts with hydrogen to form iron and steam." One is immediately faced with the problem of representing the maximum information concerning this reaction in the most concise manner; this may be done as follows.

First, write the symbols or formulas of the substances that enter into the chemical reaction (*i.e.*, the *reactants*), insert an equality sign, then write the symbols or formulas of the substances formed (*i.e.*, the *products*).



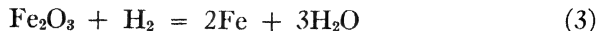
This sort of expression is sometimes called a "skeleton equation." It represents correctly the identity of each reactant and product but does not portray the correct weight relations. The latter fact is evident if one observes that expression (1) does not constitute a true equality; the total quantity of matter represented to the left of the equality sign is different from that on the right. Consequently, this expression must be adjusted (balanced) so that, in accordance with the law of conservation of mass-energy, the sum total of matter represented as products is the same as that which entered into the reaction regardless of any changes in condition of chemical combination which may have accrued in the process.

Inspection of expression (1) shows that two gram-atomic weights of iron are implicit in the formula Fe_2O_3 , but only one among the products of the reaction. There would appear to be two alternatives. To the right of the equality sign one might write Fe_2 , but this would be incorrect, because it implies the existence of a *molecule* containing two atoms of iron. The other and correct alternative is to write 2Fe , which simply suggests the formation of two gram-atomic weights of iron.

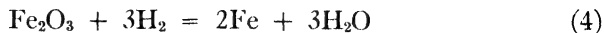


This expression is balanced with respect to iron but not with respect to oxygen. If the proposed reaction is complete (as it is) and if H_2O is the only oxygen-containing product of the reaction, then three gram-

molecular weights of water, $3\text{H}_2\text{O}$, must be formed in order to account for all of the oxygen originally present in the iron oxide. One may not write H_2O_3 because this is not the correct formula for water. Hence,



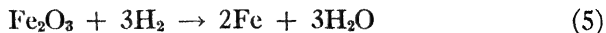
Expression (3) still needs adjustment with respect to hydrogen. On the right, $3\text{H}_2\text{O}$ requires a total of six (coefficient 3 times subscript 2) gram-atomic weights of hydrogen. This may be provided on the left by inserting a coefficient 3 before the formula H_2 ,



and (4) is a balanced chemical equation (a true equality). If, now, one adds the molecular weight of Fe_2O_3 and three times the molecular weight of H_2 , the result is exactly equal to twice the atomic weight of iron plus three times the molecular weight of steam.

An additional word about subscripts and coefficients seems in order. Subscripts are used in chemical formulas to represent numbers of atoms per molecule, and these subscripts modify only the symbols that they immediately follow. In some formulas, portions of the molecule that behave as units in chemical reactions are enclosed in parentheses followed by subscripts that apply to all that is enclosed by the parentheses. These units are called *radicals*. For example, the formula for ordinary "slaked lime" is $\text{Ca}(\text{OH})_2$, which is equivalent to CaO_2H_2 but carries the additional information that the oxygen and hydrogen constitute a radical (OH). Coefficients in chemical equations, on the other hand, denote the number of gram-molecular weights or gram-atomic weights that are involved in chemical reactions. A coefficient preceding a formula modifies *everything* in that formula; thus $3\text{H}_2\text{O}$ specifies 6 gram-atoms of hydrogen and 3 gram-atoms of oxygen.

Interpretation of Chemical Equations. Most commonly, equations are written with an arrow in place of the equality sign. The equality is still implied, and the arrow shows the direction of the chemical transformation,



i.e., a change *from* iron oxide and hydrogen *to* iron and steam. Equation (5) shows the chemical identity of each reactant and each product.

In addition, it includes all of the weight relations that are inherent in chemical symbols and formulas, as modified by the coefficients inserted during the process of balancing the equation. That is, equation (5) shows that one gram-molecular weight of Fe_2O_3 ($2 \times 55.85 + 3 \times 16.00 = 159.70$) reacts with three gram-molecular weights of hydrogen ($3 \times 2 \times 1.0080 = 6.048$) to form two gram-atomic weights of iron ($2 \times 55.85 = 111.70$) and three gram-molecular weights of steam [$3 \times (2 \times 1.0080 + 16.00) = 54.048$]. As noted previously, these numbers may be expressed in any desired units.

Although much information is included in chemical equations, some useful facts cannot be incorporated conveniently. For example, equation (5) does not specify the experimental conditions necessary for the occurrence of the indicated change. Nor does the equation tell us whether the indicated change will occur completely, *i.e.*, whether all or only a part of the iron oxide and hydrogen will be converted to iron and water.

Use of Chemical Equations. In addition to their serving as descriptions of chemical reactions, equations provide a means of obtaining much useful information by the use of simple arithmetic. Assume that we have 15 tons of an iron ore and that a chemical analysis shows that the ore contains 90 per cent Fe_2O_3 . The question is this: If we had a 100 per cent efficient process for the removal of the iron from its compound with oxygen [*e.g.*, by use of the reaction shown by equation (5)], how much iron could be produced?

First, 15 tons of the ore contains 13.5 tons of Fe_2O_3 .

$$15 \times 90\% = 13.5 \text{ tons}$$

Next, we must recognize from the weight relations shown by equation (5) that 159.70 tons of Fe_2O_3 yields 111.70 tons of iron. Because this relationship holds regardless of the quantity of Fe_2O_3 with which we start, it follows that 13.5 tons of Fe_2O_3 will yield some quantity of Fe that we will call x . The number x is related to 13.5 in the same way that 111.70 is related to 159.70; accordingly,

$$\frac{13.5}{x} = \frac{159.70}{111.70}$$

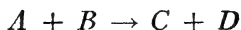
or

$$159.70x = 13.5 \times 111.70$$

and

$$\begin{aligned}x &= \frac{13.5 \times 111.70}{159.70} \\&= 9.4 \text{ tons of Fe}\end{aligned}$$

From this illustration it is clear that equations make it possible to acquire information quickly that otherwise could be had only by slow and painstaking experiments in the laboratory. If, in order to translate this specific example to a general case, we represent the two reactants in equation (5) by A and B and the two products by C and D , respectively,



it is seen that A has been used (above) as a basis for the calculation of C . We could equally well calculate the weight of D formed from the given weight of A , or the weight of B that will react with the specified quantity of A , etc. Given a chemical equation and a specified amount of any one reactant or product, one may calculate the corresponding amount of any other of the reactants or products.

EXERCISES

1. *New terms:* reactants, atomic weight, gram-molecule, synthesis, gram-atomic weight, radical, gram-molecular weight, chemical analysis, products, gram-atom.
2. What experimental information is needed in order to establish the formula for a new compound?
3. What is the chief chemical component of (a) limestone; (b) sand; (c) slaked lime?
4. If the relative atomic weight of an element is known, how may one calculate the absolute weight of an atom of that element?
5. How are symbols derived from the names of the elements?
6. Why was oxygen chosen as the standard for relative atomic weights? Why was the number 16.0000 selected?

7. If the number 4.0000 had been selected to represent the relative atomic weight of oxygen, what would be the relative weight of (a) the sulfur atom; (b) the hydrogen atom?
8. How many atoms are represented by the symbol for any element?
9. How many molecules are represented by the formula for any compound?
10. Why does the chemist ordinarily not use values for the absolute weights of the various kinds of atoms?
11. Summarize the information provided by (a) a symbol; (b) a formula.
12. With reference to chemical equations, explain clearly the function of (a) coefficients; (b) subscripts.
13. In what order are symbols written in formulas?
14. What is the molecular weight of each of the following compounds: (a) NI_3 ; (b) P_2S_5 ; (c) $\text{Cu}_3(\text{PO}_4)_2$?
15. Write formulas for compounds containing (a) three atoms of uranium and eight atoms of oxygen; (b) one atom of zinc, one atom of sulfur, and three atoms of oxygen; (c) three atoms of lead and two atoms of nitrogen.
16. Calculate the percentage of (a) Zn in ZnO ; (b) P in PBr_5 ; (c) Ag in AgNO_3 ; (d) U in $\text{UO}_2(\text{NO}_3)_2$.
17. Write equations for the following chemical changes: (a) a reaction in which sulfur and oxygen combine to form a compound having the formula SO_2 ; (b) a reaction in which SO_2 reacts with oxygen to form a compound having the formula SO_3 ; (c) a reaction in which Ag_2O is decomposed by heat to form silver and oxygen; (d) a reaction in which SnO_2 reacts with carbon to form tin and CO .
18. On the basis of the equation written in exercise 17(d) above, calculate (a) the weight of tin that could be produced from 5 lb. of SnO_2 , (b) the weight of carbon that would be required in the reaction, and (c) the weight of CO that would be produced as a by-product.
19. By use of the reaction $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$, eight grams of CaO were formed. What weight of CO_2 was formed at the same time?

COLLATERAL READING

BRISCOE: "General Chemistry for Colleges," Houghton Mifflin Company, Boston, 1943, Chapter 11.

DEMING: "General Chemistry," John Wiley & Sons, Inc., New York, 1944, Chapter 4.

RICHARDSON and SCARLETT: "General College Chemistry," Henry Holt and Company, Inc., New York, 1947, Chapter 3.

SCHÖCH, FELSING, and WATT: "General Chemistry," McGraw-Hill Book Company, Inc., New York, 1946, Chapter III.

The Nature of Atoms and Molecules

IN ACCORDANCE with ideas already considered, all forms of matter in the physical universe consist of solids, liquids, and gases that are composed of elements (either as such or in the form of compounds or mixtures). The chemical elements, in turn, are known to consist of atoms, and this leads to the question as to the composition of atoms. This progressively more detailed inquiry into the nature of matter in terms of smaller and still smaller particles reminds one of the old saying to the effect that "the little fleas have lesser fleas, and so on ad infinitum." The recognition that complex forms of matter may be resolved into successively simpler forms is a history of man's progress toward a fuller understanding of the ultimate constitution of matter. These are problems that are of mutual concern in physics and chemistry; it is truly a borderline area of knowledge. Both chemical and physical methods have been employed in the search for "fundamental particles" which are smaller than atoms (*i.e.*, *subatomic particles*) and which may be looked upon as the ultimate building stones of which atoms are made.

There is ample evidence that the atoms of the elements are not in themselves simple particles of matter. To be sure, these evidences are indirect, but they are none the less convincing. There are many different kinds of chemical changes which show that the atoms must be made up of simpler particles; there is even more conclusive evidence from certain studies that are normally considered to be in the realm of physics rather than chemistry.

Radioactivity. Since 1896, when the French physicist Becquerel (Fig. 16) discovered natural radioactivity, it has been known that at least certain kinds of atoms are capable of *spontaneous* disintegration into simpler bodies. For a long time it was thought that only the atoms

of the heavier elements such as uranium and radium (symbol Ra) are capable of this type of change. Nearly forty years later it was found that some atoms of the light elements also exhibit the property of radioactivity (see Chapter 6).

It should be emphasized at the outset that radioactive decomposition (*decay*) of atoms is a spontaneous process over which we can exert no control whatever. Much may be learned, however, through the study of processes of radioactive decay.

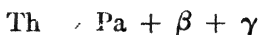


Figure 16. Antoine Henri Becquerel.
(Courtesy of the Edgar F. Smith Memorial
Collection, University of Pennsylvania.)

When a given atom decays, it changes into an atom of some other element and gives off "rays" or "particles" in the process. The uranium atom of atomic weight 238 decays to form a thorium atom (symbol Th) of atomic weight 234. Concurrent with this change is the ejection of a particle that has (by difference) a relative weight of four and that bears two units of positive charge; this is known as an *alpha particle* (symbol Greek α).



The resulting thorium atom is also radioactive and changes spontaneously to an atom of another element called protoactinium (symbol Pa) that also has an atomic weight of 234. The latter fact means that the other product of this decay must have been one having no mass or at best an exceedingly small mass. The ejected particle in this case is the *beta particle* (β), which is an electron that may be considered to be a single unit of negative electricity. (The very small mass of the beta particle may be judged from the fact that an atom of the lightest element—hydrogen—is 1845 times as heavy as a beta particle.) At the same time, energy is released in the form of *gamma radiation* (γ); gamma rays have neither mass nor charge and are similar to X-rays.



As will be shown later, other particles are formed in the process of radioactive decay. Of more immediate concern is the question of how this information may be used in arriving at an understanding of the nature of atoms. Investigations made many years ago show that the alpha particle is about four times as heavy as the hydrogen atom. This fact alone suggests that the alpha particle must be composed of still smaller units of matter, and this particle is in fact found to be made up of *neutrons* and *protons*. The neutron is an electrically neutral particle having a mass the same as the hydrogen atom. The proton bears one unit of positive charge and has a mass just a little less than that of the hydrogen atom (*i.e.*, $1844/1845 \times 1.0080$). Consequently, we may consider that a positive proton plus a negative electron is equivalent to a neutral neutron.

While it must be appreciated that the constitution of atoms is in all of its ramifications an exceedingly complex problem, these three fundamental particles (the electron, the proton, and the neutron) serve as a basis for the establishment of a useful interpretation of the structures of atoms. All three of these particles are known as products of radioactive decay; if they come from atoms, then it is reasonable to interpret the structures of atoms in terms of these particles until it can be shown that still simpler or other particles are involved.

The Structures of Atoms. For present purposes an atom may be thought of as an *electrically neutral* object which occupies a volume in space which may be considered to be spherical in shape. At the center of the sphere is a *nucleus* made up of protons and neutrons. Because of the presence of protons (each of which bears one unit of positive charge), that part of the atom called the nucleus must bear a net positive charge the magnitude of which depends upon the number of protons in the particular nucleus. This number is called the *atomic number* and is characteristic of each kind of atom.

The nucleus of the atom is known to be very small in relation to the size of the atom as a whole. The part of the atom other than the nucleus (*i.e.*, the extra-nuclear part) consists only of electrons that may be thought of as rotating in well-defined orbits about the nucleus. According to these views, the atom may be likened to a miniature solar system; and since the electrons have so little mass, the bulk of the mass of the atom must be concentrated in the central nucleus.

The element hydrogen consists of the simplest known kind of atom.

The relative weight of the hydrogen atom and the neutron are the same, but this cannot lead to the conclusion that the two are identical, for they exhibit different properties. The alternative is to conclude that the hydrogen atom consists of a proton that makes up the nucleus¹ and one electron outside of the nucleus. Such a structure may be represented (schematically) as shown in Fig. 17. In this as in all similar diagrams used in this book, the proton is represented by the letter p and the negative electron by e^- in order to distinguish between electrons that are simply parts of the extranuclear structure of atoms

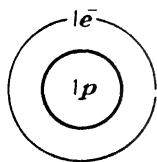


Figure 17. Diagram representing the structure of the hydrogen atom.

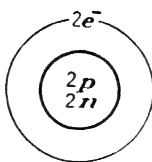


Figure 18. Diagram representing the structure of the helium atom.

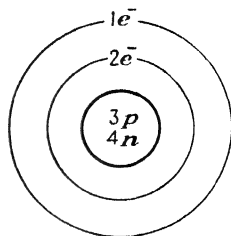


Figure 19. Diagram representing the structure of the lithium atom.

as opposed to those electrons that are given off in the process of radioactive decay. The neutron is designated by the letter n .

In order of increasing complexity, we proceed from the simplest element, hydrogen, to the element helium (symbol He), which has an atomic weight = 4 and an atomic number = 2. From the latter, it follows that there must be two protons in the helium nucleus. There must be two electrons outside of the nucleus because the atom is electrically neutral. In order to account for four units of atomic weight, the nucleus must contain two neutrons in addition to the two protons. The structure of the helium atom is therefore shown by Fig. 18.

From its atomic weight and atomic number, the lithium atom's (symbol Li) structure may be deduced similarly. The only difference is that, as shown in Fig. 19, the third electron rotates in an orbit

¹ This hydrogen nucleus is the only one that does not contain at least one neutron.

further removed from the nucleus. The orbits in which electrons rotate about the nucleus are said to be in "shells." The first such shell may contain only two electrons, but the second can accommodate eight.

The Periodic Arrangement of the Elements. In Fig. 20 there are diagrams for the structures of atoms of the elements having atomic numbers 1 to 20 inclusive. A careful inspection of these diagrams shows that the structures are arranged in vertical columns on the basis of similarity in structural details. It will be noted that in the first vertical column the structures of the hydrogen, lithium, sodium, and potassium (K) atoms are all similar in that each has one electron in the outermost shell. Similarly, in each succeeding vertical group this same kind of resemblance in structure is observed.

If these diagrams are now inspected from left to right in each horizontal row, it is seen that the diagrams are arranged *in order of increasing atomic number*. In the first horizontal row, which contains only H and He, the first shell is completed because this shell can accommodate only two electrons. The second shell can accommodate eight electrons, and these are shown in the progressive development of the structures from Li to Ne inclusive. Thereafter the development of the third shell of electrons must begin, and this leads to a periodic recurrence of structures having the features of similarity noted above.

The very important conclusion is that the structures of atoms of the elements are such that they lead to a natural and orderly classification of the elements in terms of the structures of their atoms. Although certain complications need to be taken into account, Fig. 20 may be extended to include all of the elements. If this is done using the symbols for the elements rather than the diagrams of the structures of their atoms, there results the chart shown in Fig. 21. This is called the *periodic arrangement of the elements* or the *periodic table*.

Before proceeding with a discussion of the general features of the periodic table, it seems worth while to digress and point out that the preceding discussion represents a reversal of history. Actually, the periodic arrangement of the elements was known and used prior to 1875. This was long before the discovery of such objects as neutrons and protons and certainly well in advance of the development of any really useful ideas about atomic structure. Although many scientists made significant contributions to these early developments, most of the credit goes to the Russian chemist Dimitri Ivanovich Mendelyev

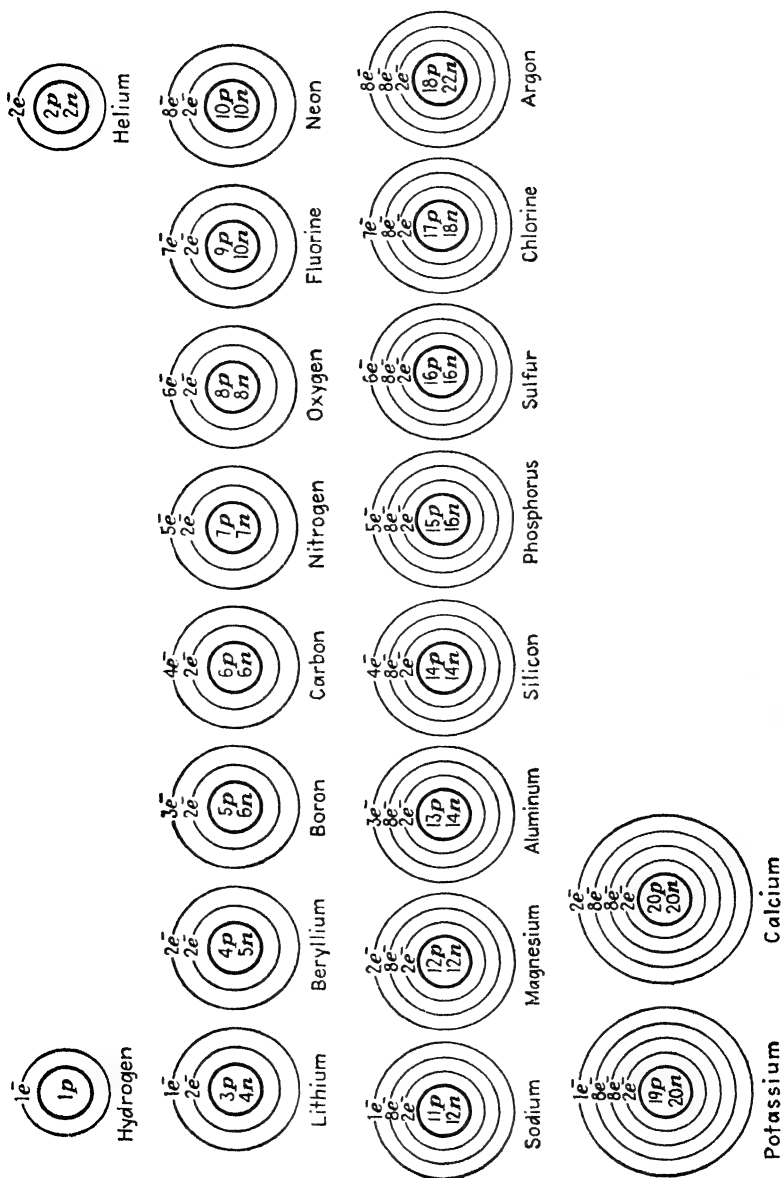


Figure 20. Diagrams representing the structures of atoms of the elements having atomic numbers 1 to 20, inclusive.

(Fig. 22). He recognized that the elements were susceptible to an orderly classification solely on the basis of the extent to which they exhibit similarities in their chemical and physical properties. He took into account also the manner in which similar elements exhibit differences. Without any real knowledge of the nature of atoms, Mendelyev devised the periodic arrangement despite the fact that many of the elements had not yet been discovered. The success of his work may be judged by the fact that, on the basis of his incomplete table,



Figure 22. D. I. Mendelyev (from a portrait painted by Mendelyev's wife). (Courtesy of the Edgar F. Smith Memorial Collection, University of Pennsylvania.)

he was able to predict with truly remarkable accuracy the properties of elements then unknown.

In the years that followed Mendelyev's classical work, the evolution of our present ideas about atomic structure was slow and came only as the result of the work of many chemists and physicists. One important discovery was followed by another and still another; but these were often apparently unrelated, or their interrelationship was obscure. As new knowledge was added to the old, it became possible to fit together the various experimental facts and mold them into a consistent pattern. These developments constitute one of the most inspiring chapters in the history of the physical sciences, but space will not permit further elaboration here. Among the many famous

scientists who made noteworthy contributions, the English physicists Moseley, Chadwick, and Rutherford; the Danish chemist Bohr; and the American chemists G. N. Lewis (of the University of California) and Irving Langmuir (of the General Electric Co.) are outstanding.

Some Features of the Periodic Table. By way of review it should be recalled that (1) the atomic number of an element represents the net positive charge (= number of protons) of the nucleus; (2) the atoms of the elements are electrically neutral bodies; and (3) a consequence of (1) and (2) is that the atomic number designates also the number of electrons in a neutral atom. Since the chemical properties are determined by the number and disposition of the electrons in relation to the nucleus, it follows that these properties are dependent upon (*i.e.*, a function of) the atomic number. This number also defines the nature of the nucleus, and this is the part of the atom which largely determines physical properties—at least those which are dependent upon mass. This dependence of both chemical and physical properties upon the atomic number is expressed by the *periodic law*, which is: *The properties of the elements are periodic functions of their atomic numbers.*

The periodic recurrence of structural similarity referred to previously leads to tabulations like that shown in Fig. 21. The vertical groups of elements comprise those having similar (but not identical) structures; consequently they have similar (but not identical) chemical and physical properties. The elements of Group 0 (the “inert gases”) all have completed structures. That is, all shells contain their respective maximum numbers of electrons, and this is reflected in their great chemical stability. As a result, these elements do not take part in ordinary chemical reactions; but because their weights increase progressively from atomic number 2 to atomic number 86, they do show typical *trends* in physical properties that are dependent upon mass. The elements of Groups I and II include elements that have one and two electrons, respectively, in their outermost shells. These, like all others that have shells deficient in electrons, take part in chemical reactions in a manner that will be discussed shortly.

The periodic arrangement of the elements is the basis for the classification, organization, and correlation of much of the information in the field of *inorganic chemistry*. A knowledge of the properties of two

elements in a given group or sub-group¹ enables one to predict the properties of the others. If it is found experimentally that Si and Ge both form the same type of compound with oxygen (that is, SiO_2 and GeO_2), it may be anticipated that C, Sn, and Pb will form similar compounds and they do. If, in Group VII, HBr is found to be less stable than HCl, one would predict that HF would be more stable than HCl and that HI and HAt are successively less stable than HBr. Again, this is in accord with the known facts. Similar trends in properties are exhibited by the elements of each group.

Useful relationships are portrayed also by the segregation of the elements into horizontal rows (*periods*). It will be recalled from preceding discussions that the trend from left to right corresponds to the progressive addition of electrons as each shell approaches the acquisition of its maximum number. This, of course, results in chemical and physical dissimilarities, but it also establishes *trends* in properties. It is a matter of considerable convenience that the periodic table provides a rough basis for the separation of the elements in terms of the extent to which they exhibit the properties that are characteristic of metals. Excluding the inert gases, the diagonal line drawn through Fig. 21 is intended to show this relation. The most metallic elements lie below and to the left of the line; the most non-metallic elements lie above and to the right of the line (with the exception of the metals of Group VIII). The elements that lie on or near the line exhibit properties that are intermediate—*i.e.*, partially metallic and partially non-metallic—and hence are called semi-metals or metalloids.

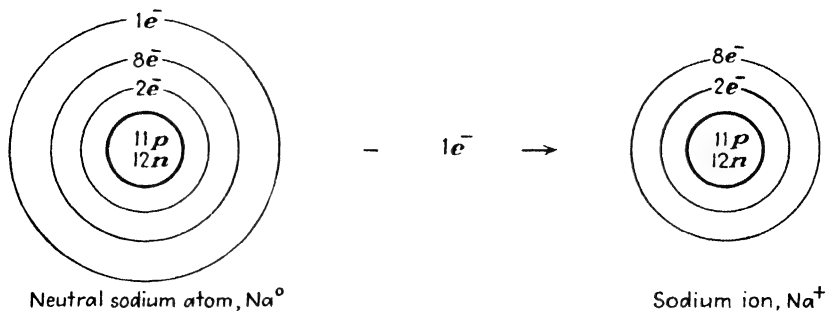
The elements that are listed below the main body of the table in Fig. 21 and designated as rare-earth elements are ones that are typically set apart because they are otherwise only inconveniently tabulated. The structures of the atoms that are involved are nevertheless consistent with the over-all pattern of the periodic table.

The Nature of Chemical Changes. A beginning may be made toward an understanding of the manner in which atoms combine during chemical reactions by considering the structures of other atoms in relation to the inert gases. It is a broad general principle that matter

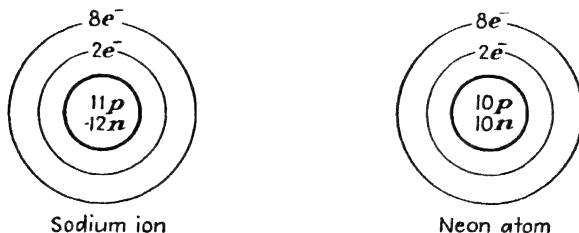
¹ Each vertical group is subdivided into a main group and a sub-group. For example, C, Si, Ge, Sn, and Pb constitute the main group in Group IV, while the sub-group consists of Tl, Zr, and Hf. Such subdivision within a group is made on the basis of the structural details of the atoms concerned.

tends to exist in a condition of maximum stability. Accordingly, when atoms participate in chemical reactions, they do so in a manner that will permit them to achieve extranuclear structures similar to those of the stable inert gases.

Ordinary table salt (sodium chloride, NaCl) may be formed by the direct union of the elements sodium and chlorine. The question is, *how* and *why* do these two elements combine? The sodium atom (periodic Group I) has one electron in its outermost shell. If the sodium atom



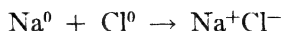
could lose this one electron, the remainder is an *ion*, specifically a sodium ion. This ion contains eleven protons and only ten electrons and consequently has a positive charge of one unit; this is indicated most simply by writing Na^+ . If, now, we compare the structure of the sodium ion with that of the atom of neon (the inert gas that stands nearest to sodium in the periodic table), it is seen that the loss of one electron by the sodium atom results in an ion having an extra-



nuclear structure like that of the stable neon atom. Of course, the two shown above differ within the nucleus, and one bears a positive charge, while the other is electrically neutral; the properties of the two must therefore differ. Nevertheless, the sodium ion represents the

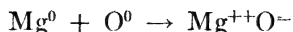
sodium atom's nearest approach to the stable neon structure without alteration of the nucleus.

In a wholly analogous manner it may be shown that the chlorine atom (periodic Group VII) with seven electrons in its outermost shell may—by acquiring one electron—achieve an extranuclear structure like that of the nearest inert gas, argon. When the neutral chlorine atom gains this one electron, it thereafter has one more electron than protons and consequently bears one unit of negative charge. The chlorine atom becomes a negative *chloride ion*, Cl^- . The union of atoms of sodium and chlorine to form sodium chloride may be represented simply as,

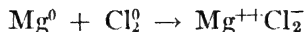


where the superscript zero indicates a neutral atom and the superscript plus and minus signs indicate the charges on the ions. The sodium and chloride ions may be thought of as being held together by the electrostatic attraction of their unlike charges.

In a like manner, the magnesium atom (periodic Group II) may lose two electrons and the oxygen atom (periodic Group VI) may gain two electrons and thereby achieve structures like the inert gas neon when these two elements combine to form the compound, magnesium oxide ("magnesia"),



and the same sort of change is involved in the formation of magnesium chloride,



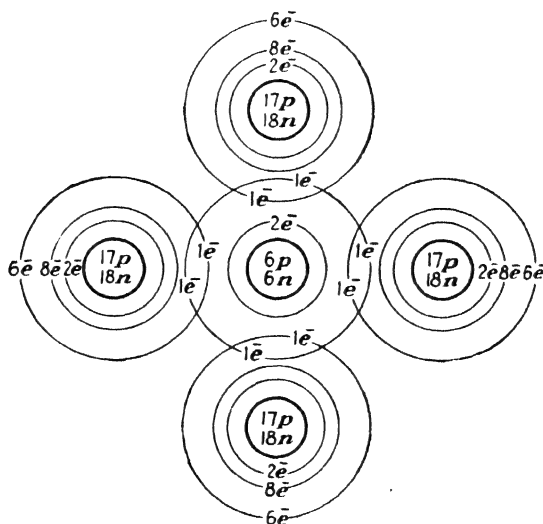
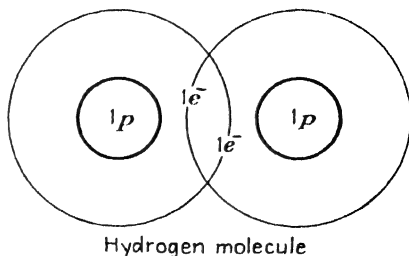
a change in which the magnesium atom loses two electrons and each chlorine atom gains one. *Compounds that are formed by loss and gain of electrons are called ionic compounds.*

Another mode of compound formation involves, not the loss and gain, but rather the *sharing of electrons*. In its simplest application, two electrons, one from each of two atoms, form an electron pair that functions simultaneously in the outermost shells of both atoms. The two shells may be thought of as "overlapping," as shown below for the hydrogen molecule, H_2 . Since each atom now has effectively two electrons, each has achieved a structure similar to the stable helium

atom. The chlorine molecule, Cl_2 , may be represented diagrammatically in the same way; but to represent the oxygen molecule, O_2 , requires that a total of four electrons (two from each oxygen atom) must be shared in order that each may approach the neon structure.

An illustration of the sharing of electrons between atoms of unlike elements is provided by the following diagram for the carbon tetrachloride molecule [*i.e.*, the familiar "carbon tet" used in fire extinguishers and otherwise (Chapter 26)].

It is evident that compound formation by sharing of electrons does not result in the formation of ions. In order to distinguish, *compounds that are formed by the sharing of electrons are called covalent compounds.*



Interpretation of compound formation in terms of loss and gain or sharing of electrons would represent an over-all simplification were it not for two additional facts. First, most compounds are formed not by loss and gain of electrons or the sharing of electrons but rather by a combination of these two processes. Such intermediate cases are, of

course, difficult to show diagrammatically. Second, the elements do not show any wholly consistent preference for one process or the other. If element X combines with Y largely by loss and gain of electrons, X may well combine with Z largely by sharing. Here, we need only recognize that ionic compounds are formed most commonly by elements that must either lose or gain only a small number of electrons in order to achieve inert-gas structures. The larger the number of electrons, which must be gained, lost, or shared, the greater will be the probability of chemical union by sharing. There are indeed many exceptions to these purely qualitative generalizations.

Valence. An understanding of the nature of chemical changes provides a logical answer to a question that inevitably arises when students first encounter chemical formulas. Why is it that, for example, *two* atoms of sodium combine with one of oxygen in Na_2O , while there is only *one* atom of magnesium per atom of oxygen in MgO ? The answer is evident when it is recalled that oxygen tends to gain two electrons and each sodium atom (Group I) loses only one; hence two atoms of Na are required to supply the two electrons needed. One magnesium atom (Group II), however, can lose two electrons, and thus only one atom of magnesium is required.

The term *valence* came into use long before chemists knew much about the true nature of atoms and was used to describe what might be called a measure of "combining capacity." Now, we distinguish in terms of the process involved and specify that the *electrovalence* of an element is the number of electrons lost or gained, while the *covalence* of an element is the number of *electron pairs* shared. In the ionic compound, $\text{Mg}^{++}\text{Cl}_2^-$, the electrovalence of Mg = 2 and that of Cl = 1. In the covalent compound CCl_4 , the covalence of C = 4, that of Cl = 1. As will be seen later, valence is not a specific property; although each element has one particular valence that it exhibits most commonly, many elements exhibit more than one valence in their various compounds.

The concept of valence is useful in writing the formulas or compounds. Suppose that we know that the electrovalence of aluminum is three while that of iodine is one. From this information one may directly write the formula, AlI_3 . Similarly, valence may be deduced from formulas. Given the formula SiO_2 , if one remembers that the

valence of oxygen is two, it follows that the valence of Si in SiO_2 must be four.

Except for pictorial representations of atoms and molecules, this chapter is concerned almost entirely with the extranuclear properties of atoms. The chapter that follows is concerned with chemical changes that involve alterations in the nucleus of the atom.

EXERCISES

1. *New terms:* covalent compound, radioactivity, ion, atomic number, beta particle, electrovalence, gamma ray, neutron, ionic compound, electron, alpha particle, nucleus, proton, covalence, periodic table.
2. State the periodic law.
3. Why do the "inert gases" not form compounds as do the other elements?
4. What is the difference between an electron and a beta particle?
5. Given the information that the valence of $\text{H} = 1$, $\text{Na} = 1$, $\text{Br} = 1$, and $\text{O} = 2$, what is the valence of the underscored element in each of the following formulas: (a) NH_3 , (b) SiBr_4 , (c) $\text{Na}_2\underline{\text{S}}_2$, (d) $\text{Zn}\underline{\text{O}}$, (e) $\underline{\text{Bi}}_2\text{O}_3$, (f) $\text{S}\underline{\text{O}}_3$, (g) $\text{Ca}\underline{\text{H}}_2$, (h) $\text{Ca}_3\underline{\text{P}}_2$, (i) $\underline{\text{Cu}}_2\text{S}$, (j) $\underline{\text{SiC}}$?
6. Draw a diagram showing *only the nucleus* of the helium atom (at. wt. = 4, at. no. = 2), and compare this diagram with the information given concerning the alpha particle. What conclusion may be drawn?
7. What determines the chemical properties of any element?
8. If the electrovalence of the metal zinc is two and that of fluorine is one, write the formula for the ionic compound that these two elements would be expected to form.
9. If the covalence of hydrogen and fluorine is one in each case, write the formula for the anticipated covalent compound of these two elements.
10. Justify the view that there are *three* possible modes of compound formation.
11. Write the formula for the covalent compound of carbon and oxygen in which the covalences of the elements are four and two, respectively.

12. Without reference to any of the diagrams given in this chapter, draw diagrams for (a) the sulfur atom (at. wt. = 32, at. no. = 16), (b) the aluminum atom (at. wt. = 27, at. no. = 13), (c) the aluminum ion (at. wt. = 27, at. no. = 13), (d) the carbide ion (at. wt. = 12, at. no. = 6), (e) the covalent water molecule (at. wts., H = 1, O = 16; at. nos., H = 1, O = 8), (f) the covalent molecule NH_3 (at. wts., N = 14, H = 1; at. nos., N = 7, H = 1).
13. With reference to the periodic table, locate the metals, the inert gases, the metalloids, and the non-metals.
14. Write the formula for the ionic compound of sodium and oxygen in which the electrovalences are one and two, respectively.
15. What tendencies are being exhibited when atoms lose, gain, or share electrons?

COLLATERAL READING

PAULING: "General Chemistry," W. H. Freeman and Co., San Francisco, 1947, Chapters 4, 5, and 6.

RICHARDSON and SCARLETT: "General College Chemistry," Henry Holt and Company, Inc., New York, 1947, Chapters 4, 5, and 6.

SCHOCH, FELSING, and WATT: "General Chemistry," McGraw-Hill Book Company, Inc., New York, 1946, Chapters XIII, XIV, and XV.

Artificial Radioactivity and Atomic Energy

It is NO exaggeration to state that new discoveries concerned with radioactive elements and the successful utilization of atomic energy have ushered in a new era in the history of civilization. Substantially every phase of the future of mankind, including the very question as to whether mankind is to have a future of the sort we should wish, is intimately interwoven with these recent advances in scientific knowledge and others that will inevitably follow. The full impact of these developments has dawned only slowly and incompletely upon the consciousness of the average citizen, who has been understandably confused by a maze of technical details and some well-meaning but unfortunately extreme predictions calculated to arouse interest at any cost. While there is no wish here to underemphasize either the magnitude or the importance of the attendant problems of public education, it seems self-evident that a well-informed public opinion can accrue only on the basis of at least a rudimentary understanding of a few simple scientific principles. At the risk of error inherent in oversimplification, the discussion that follows represents an effort to provide such a basis.

Products of Radioactive Decay. Before proceeding with the main objectives of this chapter it is necessary to inquire further into the nature of the various products formed during radioactive decay. It has already been pointed out that the decay of naturally radioactive uranium leads to radioactive thorium and this, in turn, to radioactive protoactinium. This particular sequence of decays does not stop at protoactinium but continues as shown in Fig. 23. In this figure, each circle may be thought of as representing the *nucleus* of an atom of the kind specified by the symbol and atomic weight enclosed within the cir-

cle. The horizontal arrows show the succession of radioactive changes, while the arrows pointing upward to the right denote the principal particle ejected from the decaying nucleus (gamma radiations omitted). Below each circle is given the common (and older) name of the radioactive species together with the *period of half-life*, which is the period of time required for one-half of any given quantity of that particular kind of matter to undergo radioactive decay (y, d, m, and s represent

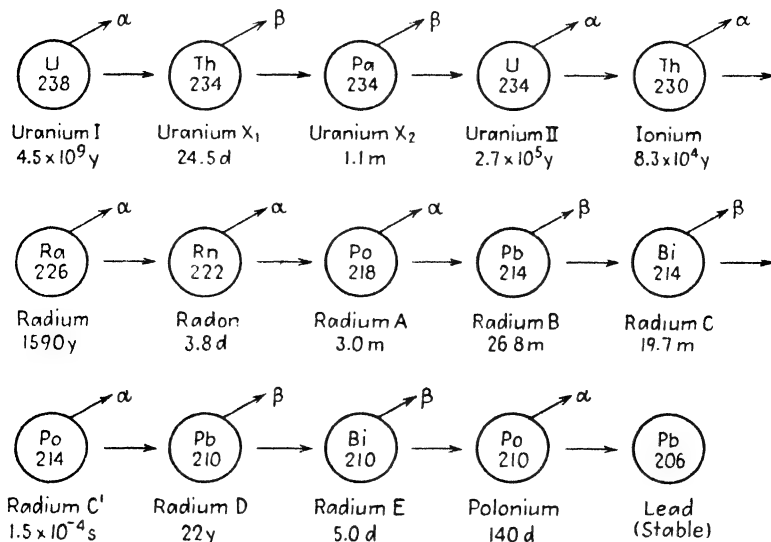


Figure 23. The uranium decay series.

years, days, minutes, and seconds, respectively). If, for example, we had exactly one pound of pure "Radium D," at the end of 22 years there would remain exactly one-half pound (the other half having decayed). At the end of a second half-life period of 22 years, there would remain exactly one-fourth pound; at the end of the next period, one-eighth pound, and successively one-sixteenth, one thirty-second, one sixty-fourth, etc. Thus it is evident that such processes of decay are never complete, but for practical purposes it is usually considered that the quantity remaining after ten half-life periods have elapsed is negligible.

It may be seen from Fig. 23 that the sequence of changes beginning with uranium involves fourteen distinct decay processes ending finally

in non-radioactive (stable) lead. The particular number of successive steps in different "decay series" varies considerably and may involve only one or several steps. There are two other natural decay series that end also in stable lead, while still another terminates in stable bismuth.

Isotopes. Figure 23 shows also that the "uranium decay series" includes two different kinds of uranium atoms, *i.e.*, those having atomic weights (*mass numbers*) of 238 and 234. Similarly, the series includes two kinds of thorium atoms, three kinds of polonium atoms, etc. The two kinds of uranium atoms differ only by four units in mass; both have the same atomic number (92) and hence have the same number of protons inside and the same number and arrangement of electrons outside of the nucleus. Consequently, these two species are identical chemically, but one contains four more neutrons in the nucleus than the other. Atoms having the same atomic number but different atomic weight are called *isotopes*. In work concerned with specific isotopes it is conventional to represent the atomic number as a left subscript and the mass number as a right superscript, for example, ${}_{92}\text{U}^{238}$ and ${}_{92}\text{U}^{234}$.

Most of the natural elements consist of two or more isotopes, and from this fact it follows that the atoms of a given kind of element are not necessarily identical. Nevertheless, the atoms of any particular kind of element all have one thing in common; they all have the same atomic number and the same number and arrangement of electrons outside of the nucleus (this, of course, is necessary if they are to be chemically identical). These facts now make it possible to define the term *element* in wholly unambiguous language: **An element is a substance made up of atoms having the same atomic number.**

The natural element hydrogen consists of two isotopes having mass numbers of one and two.¹ A third isotope that is radioactive and has a mass number of three is also known. These three isotopes (as shown in Fig. 24) are among the very few that are given special names and symbols. Deuterium is present in ordinary hydrogen only to an extent sufficient to raise the atomic weight from 1.0000 to 1.0080. In ordinary water, H_2O , the corresponding deuterium compound, D_2O , which is

¹ The mass numbers of isotopes are represented here as whole numbers. For reasons of negligible importance so far as the present discussions are concerned, the mass numbers are not exactly whole numbers but deviate therefrom only slightly.

called "heavy water," is present to the extent of 1 part in 6000. Nevertheless, methods for the separation of D_2O have been devised, and the pure compound is readily available commercially. The cost, incidentally, is approximately \$135 per pound.¹ Because the molecular

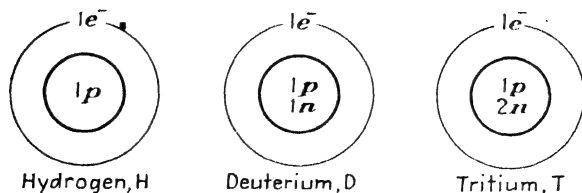


Figure 24. Isotopes of hydrogen.

weight of D_2O (20) is greater than that of H_2O (18), these two varieties of water exhibit corresponding differences in *physical* properties.

The three natural isotopes of uranium are shown in Fig. 25 together with the percentages in which they occur in natural uranium. These diagrams are simplified to the extent of representing only the total

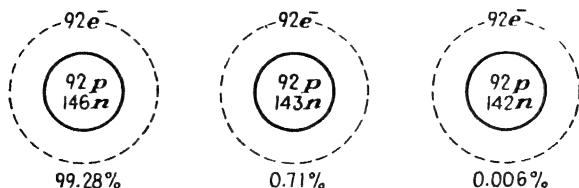


Figure 25. Natural isotopes of uranium.

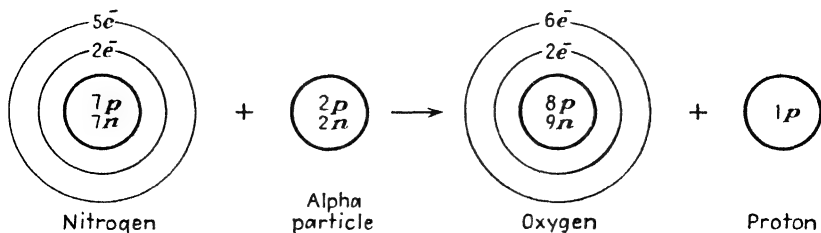
number of electrons outside of the nucleus without showing their distribution among the various shells. The importance of these isotopes will be apparent in the light of subsequent discussions.

The existence of isotopes has an important bearing upon the law of constant composition. In Chapter 3, this law was presented in language that implied no exceptions because it was deemed unwise to suggest exceptions until a basis for their explanation could be developed. The point is that the percentage composition of a pure compound depends upon whether it is made from a natural mixture of isotopes of the elements concerned or from specific isotopes. It should be quite evident that the percentage composition of H_2O (89 per cent oxygen) and

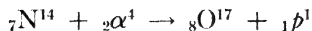
¹ Price current in 1948.

D₂O (80 per cent oxygen) differ considerably even though the two kinds of water have the same chemical properties. With but very few exceptions, the law of constant composition remains valid whenever compounds are made from elements taken from natural sources.

Artificial Radioactivity. As noted earlier, the alchemists sought quite unsuccessfully to accomplish a transmutation of base metals into gold. Although gold was not involved in any way, the first successful "transmutation" was accomplished in the year 1919, when the English physicist Rutherford performed a classical experiment that may be said to mark the beginning of a "modern alchemy" that has indeed witnessed the production of isotopes of gold from metals such as mercury, platinum, and thallium. Rutherford devised conditions favorable to a reaction between nitrogen atoms and alpha particles that produced atoms of a *stable* isotope of oxygen, and protons. This reaction may be represented diagrammatically as

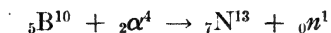


or in the form of a more or less typical chemical equation.



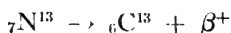
It should be noted that in this, as in any chemical equation, the sum of the mass numbers on the left of the arrow is equal to the sum of those on the right; the same must be true of the atomic numbers as well.

In 1934, Frédéric and Irène Curie Joliot carried out a similar reaction but one which differed in that the product element was *radioactive*. The reaction was that between boron atoms and alpha particles to form neutrons and atoms of a radioactive isotope of nitrogen.



The significance of this discovery of *artificial radioactivity* can scarcely be overemphasized. Of course, natural radioactivity was well known

in 1934, but little credence had been given to the possibility of man's producing in the laboratory atoms that possess the property of radioactivity. The radioactive nitrogen formed as indicated was found to decay by the emission of positive electrons (symbolized by β^+ , and also called *positrons*) to form *stable* carbon atoms of mass 13,



with a half-life period of 9.93 minutes. This kind of nitrogen does not exist in nature; for the first time man had produced not only a kind of atom not provided by nature but in addition a kind that was radioactive.

Production of Radioactive Isotopes. Transformations typified by those effected first by Rutherford and the Joliotis differ in certain respects from ordinary chemical reactions. Because the former involve changes in the nucleus of the atom, they are called nuclear reactions or nuclear transformations. Nuclear reactions are characterized by the fact that the reacting atoms undergo changes in atomic number, while this is not so for ordinary chemical reactions that involve only the electrons that are outside of the nucleus. Also, the energy changes associated with nuclear reactions are of the order of a million times greater than those involved in ordinary reactions.

The problem of bringing about nuclear transformations requires certain considerations of energy relationships that may be treated here in very general terms. Rutherford's transmutation of nitrogen and the production of artificially radioactive nitrogen both employed natural alpha particles from the decay of radium. It is helpful to think of the ${}_7\text{N}^{14}$ or ${}_5\text{B}^{10}$ nucleus as a target and the radium alpha particles as bullets or projectiles being fired just as one fires bullets from a gun at a target. Now, a necessary condition for the occurrence of a nuclear transformation is that the bullet must score a "bullseye," *i.e.*, the alpha particle must suffer a direct collision with the ${}_7\text{N}^{14}$ nucleus. Both this nucleus and the alpha particle bear positive charges, accordingly they tend to repel each other, and from this it follows that a collision of the two is rather improbable. Actually, if one employs 10,000 alpha particles, it may be anticipated that (on an average) only one will strike the target nucleus and cause a nuclear reaction. This again focuses attention upon the differences between nuclear changes and ordinary chemical reactions. If, by way of contrast, we use 10,000 atoms of oxygen in a reaction with hydrogen to form water, we expect every

one of these atoms to react to form the desired product. The comparison may be amplified by characterizing ordinary reactions as ones from which we normally expect high "yields" of the desired products, while just the reverse is true of nuclear reactions.

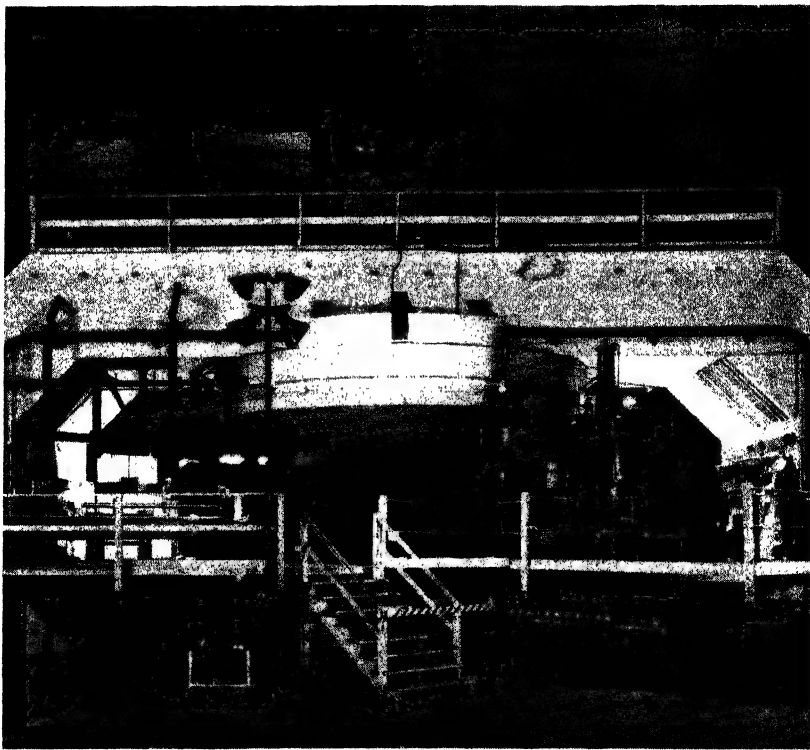


Figure 26. The 184-in. cyclotron located at the University of California. (Courtesy of Donald Cooksey and the Radiation Laboratory, University of California.)

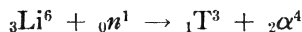
A limiting factor in the effectiveness of natural alpha particles in producing nuclear transformations is their typically low energies. If means could be found to increase the energy of such particles—to *accelerate* them to high velocities—their effectiveness in penetrating the repulsive force of positive target nuclei would be greatly enhanced. This has been accomplished by means of several different kinds of accelerating machines, among which the *cyclotron* (Fig. 26) invented in 1932 by Professor E. O. Lawrence of the University of California is that most widely known. Most natural alpha particles have energies

of the order of 5 to 6 Mev¹; by means of a cyclotron, alpha particles may be accelerated to energies of the order of 400 Mev.

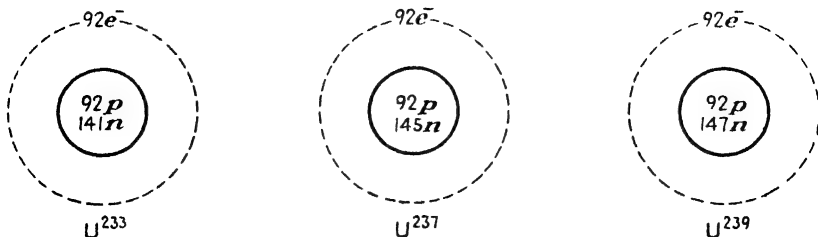
In carrying out nuclear reactions one is by no means limited to the use of alpha particles. Equally or more common is the use of protons, or deuterons (deuterium ions, *d*) accelerated in a machine such as the cyclotron, or electrons accelerated by means of the *betatron*, or even by the use of high-energy gamma rays. Alternatively, one may use neutrons that are products of certain nuclear reactions to bring about still other reactions. The neutron possesses a distinct advantage in that it is electrically neutral and hence is not repelled by either the positive target nucleus or its extranuclear electrons. An old but still useful procedure is to mix radium with beryllium in order to secure a source of neutrons. The natural alpha particles from the decay of radium react with the beryllium to provide neutrons.



The use of these different "subatomic bullets" in the bombardment of all sorts of elements and compounds has provided a wealth of new and useful radioactive isotopes. In a period of approximately fifteen years, one or (usually) more active isotopes of every known element have been produced artificially in the laboratory. At present there are several hundred known radioactive isotopes, and additional ones are being discovered almost daily. The various ways in which these are useful will be discussed later; at this point attention is called to the formation of tritium,

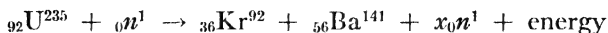


and to the fact that, in addition to the three natural isotopes of uranium, three others have been produced artificially, *i.e.*,



¹ Mev is the abbreviation for one million electron-volts. One electron-volt is the energy acquired by an electron in traversing a potential difference of one volt and is equivalent to 23,053 calories.

Nuclear Fission. Another important source of radioactive isotopes is a process that was discovered as an indirect result of work on the use of neutrons in bringing about nuclear reactions. The Italian physicist Fermi¹ discovered a variety of new nuclear reactions by bombarding many different elements (including uranium) with neutrons. His work employing uranium was repeated and extended by the German chemists Hahn and Strassman. In 1939 they made a discovery that is unlikely to be rivaled in importance by any scientific advance of the twentieth century, *i.e.*, the process of nuclear fission. In the course of their work they were able to show that the interaction of a neutron with an atom of U^{235} causes the latter to cleave into two smaller fragments.



From this equation (which is only illustrative) it may be seen that the cleavage (*fission*) of the U^{235} nucleus produces isotopes of two lighter elements. These product isotopes are radioactive; and because the fission of the U^{235} nucleus may and does occur in many different ways, these fission reactions produce a wide variety of active isotopes of lighter elements. Many of these have been isolated, identified, and put to use.

Also evident from the foregoing equation is the fact that a change induced by neutrons produces neutrons. In this equation, the number of neutrons produced per fission is indicated by x , and for present purposes we may say that the average value for x (taking into account the many ways in which uranium fission may occur) is three. Now, if one adds the total mass represented by product neutrons and the mass numbers of the two radioactive product isotopes (Kr and Ba in this case), the sum is found to be less than the sum of the masses of the two reactants. This means that, in the process of fission, *mass is converted to energy*, and this is the reason for including an energy term in the fission equation. As will be shown later, the U^{235} nucleus is not the only one that is capable of participation in the process of nuclear fission.

Atomic Energy. The energy that is made available as a product of nuclear fission is that known popularly as atomic energy but more properly designated *nuclear energy* because of its origin in atomic

¹ Now professor of physics at the University of Chicago.

nuclei. From the average loss in mass during fission, it may be calculated by means of the Einstein equation,

$$E = mc^2$$

that the energy release per fission is of the order of two hundred million electron-volts (200 Mev), or approximately 4,600,000 calories. This implies the availability of quantities of energy so vast

that it places at man's disposal not only an unprecedented source of energy but also the means for his potential destruction if unwisely used.

The fission of one or a few isolated U^{235} nuclei is in itself a relatively unimportant event. In order to take advantage of the fission process as a source of energy it is necessary to devise conditions favorable to a succession of fission reactions. This

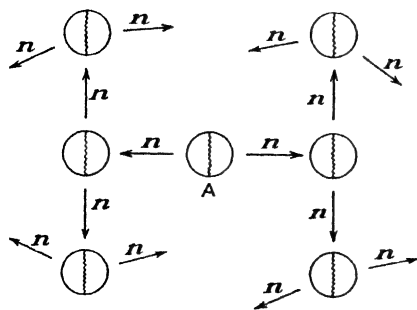


Figure 27. Diagram representing the propagation of a self-sustaining nuclear chain reaction.

of course suggests the possibility of establishing conditions such that one fission will induce others, these in turn cause still more fissions to occur, etc., and thus achieve a continuing succession of these reactions.

It has been shown how fission may be induced by neutrons; an additional piece of information of major importance is the fact that fission is also a spontaneous natural process. That is, U^{235} atoms sometimes undergo fission without being acted upon by any outside agency. Although such events are singularly uncommon in relation to all of the atoms available, ideally only one such change need occur in order to initiate a series of fissions. Let us imagine that we have a sphere of pure metallic uranium and that one U^{235} atom (labeled *A*) near the center undergoes a spontaneous fission that produces two neutrons. These two may collide with other neighboring U^{235} nuclei and induce fission as represented in Fig. 27. This idealized picture, which unwarrantedly assumes 100 per cent efficient use of all product neutrons, shows how one spontaneous fission may give rise to a

whole sequence of induced fissions. This is the kind of change that is commonly called a *self-sustaining* or *self-propagating nuclear chain reaction*.

Long before the discovery of fission, the possibility of realizing and controlling this type of mass-energy conversion was a common topic of speculation among scientists. Those whose opinions were most respected took an exceedingly dim view of the prospects for success, and anyone bold enough to express optimism was likely to become the object of more or less polite ridicule. The discovery of fission, however, provided the necessary approach, and under the impetus of war-born necessity scientists were quick to exploit the potentialities that were offered.

The Military Application of Atomic Energy. Since the initial use of atomic energy was the atomic bomb of World War II, this aspect will be considered first.

It must now be recalled that the uranium found in nature consists of 99.28 per cent U^{238} , only 0.71 per cent U^{235} , and the remainder, 0.006 per cent U^{234} . Now it so happens that U^{238} atoms *capture* neutrons without undergoing fission. Because in natural uranium there are about 140 U^{238} atoms for every one U^{235} atom, the neutrons formed by spontaneous fission of the latter would most likely be captured by U^{238} and thus have little chance to induce fission in other U^{235} atoms and initiate a chain reaction. Consequently, the use of U^{235} as a source of atomic energy requires that it be separated from all or most of the U^{238} as well as from any impurities which might capture neutrons. This poses an especially difficult problem because all kinds of uranium atoms are chemically identical (they all have the same extranuclear structure) and cannot be separated by chemical means. Furthermore, separation by physical methods is rendered exceptionally difficult by the very small difference in the masses of the U^{235} and U^{238} isotopes. Notwithstanding what appeared to be almost insurmountable obstacles, several quite different methods were devised with varying degrees of success, and two of these were put into large-scale plant operation at Oak Ridge, Tenn. (Fig. 28), during the latter years of World War II. The Oak Ridge plant produced the U^{235} employed at Los Alamos, N.M., in the manufacture of the atomic bomb dropped on Hiroshima in August, 1945 (Fig. 29).

There appeared yet another approach to the utilization of nuclear energy, and this was based upon the fact that U^{238} atoms capture neu-

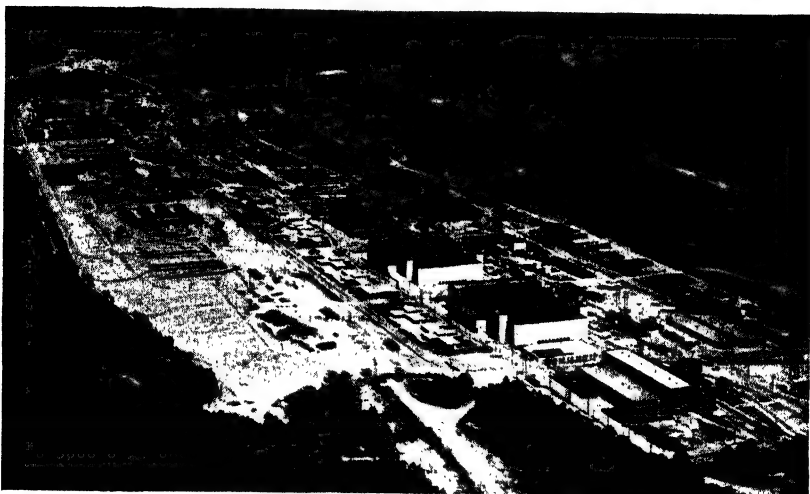
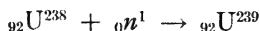


Figure 28. One of the Oak Ridge, Tenn. production plants in which uranium isotope separation was accomplished. (Courtesy of The Atomic Energy Commission.)

trons. In 1939, McMillan and Abelson showed that bombardment of U^{238} atoms with neutrons leads to the formation of U^{239} ,



which is also radioactive and decays with a half-life period of 23 minutes by emission of beta particles to form a new element that they named neptunium (symbol Np),



This discovery was confirmed by Seaborg and co-workers at the University of California in 1940. Further, they found that Np^{239} also decays by beta-particle emission with a half-life of 2.33 days to form another new element that they named plutonium (symbol Pu),



These discoveries were of major significance because they represented the production of new elements in the laboratory. The old idea that



Figure 29. Atomic-bomb destruction at Hiroshima, Japan (U.S. Air Force Photo.) (Courtesy of *The Atomic Energy Commission*.)

there could be only ninety-two elements was thrown into the discard. The plutonium isotope Pu^{239} was of interest for other reasons; it is of long half-life (24,300 years) and like U^{235} is a fissionable isotope. Accordingly, it was of promise as a source of nuclear energy if means for its production could be devised.

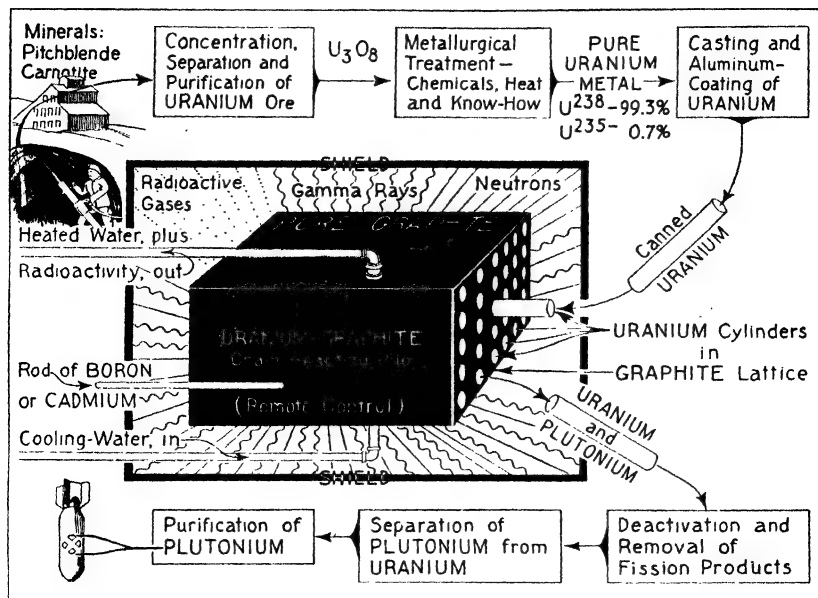


Figure 30. The production of plutonium. (Courtesy of *The Petroleum Engineer* and Professor Clark Goodman, Massachusetts Institute of Technology.)

The production of plutonium is accomplished by the use of the *chain-reacting pile*, Fig. 30, and employs natural uranium. Because U^{238} atoms can capture neutrons only if they have energies within a certain (low) range, it is necessary to provide an interlacing structure composed of uranium together with a *moderator*. The latter must be made up of atoms which do not capture neutrons (*e.g.*, graphite, heavy water, etc.) but with which the neutrons from U^{235} fission may collide, lose energy, and be "slowed down" to energies such that their capture by U^{238} may occur.

Perhaps the chain-reacting pile may be understood better in terms of a greatly simplified experiment. Suppose that we have a supply of uranium metal and graphite, both in pieces the size and shape of

ordinary building bricks. Suppose further that we build a cube one yard on the edge, using alternating bricks of uranium and graphite. A chain reaction would not go on in this structure since, owing to its small size, too many neutrons would escape into the surrounding atmosphere. If, however, we continue to increase the size of the structure and arrange the bricks in a geometric pattern designed to achieve the most effective use of the moderator, we shall ultimately build a pile to the so-called "critical size," *i.e.*, one so large that some loss of neutrons can be tolerated and yet enough be retained to keep the chain reaction going. One may now legitimately wonder (particularly in view of Fig. 27) why a chain reaction once initiated in a pile does not continue self-propagation and get out of hand. The answer is simple in principle but complex in practice. The pile is provided with *control rods* made of cadmium or of some other material that has a pronounced tendency to capture neutrons. By inserting these rods into the pile to the desired depth, the rate of propagation of the reaction may be controlled, and this provides also a means of stopping the pile operation completely should that be desired.

The massive chain-reacting piles that were constructed at the Hanford Engineer Works near Pasco, Wash. (Fig. 31), during World War II employ graphite as the moderator and proved capable of producing efficiently quantities of plutonium that were indeed large, but of a magnitude that cannot now be revealed. The metal removed from the piles contains much unchanged uranium, some neptunium and plutonium, and a whole array of radioactive fission products. Separation of the fissionable Pu^{239} in this case enjoys a distinct advantage over the separation of U^{235} from U^{238} . For the reason that Pu^{239} differs chemically from uranium, neptunium, and the fission products, the plutonium may be separated by purely *chemical* methods. Even so, the chemical separation of plutonium is quite complicated, and the details remain one of the most carefully guarded secrets of the wartime atomic-energy program.

In order to appreciate the nature of the chemical problem, one must remember that the mixture which comes from the pile is composed largely of radioactive materials which give off gamma rays and alpha and beta particles. The specific properties of alpha and beta particles and more particularly of gamma rays necessitate certain precautions in almost any work involving radioactive isotopes. Alpha particles are

ejected from decaying nuclei with relatively low energies; this, together with their relatively large mass, means that even the most energetic alpha particles are not very penetrating. Alpha particles travel at velocities approximating only 10,000 miles per second and can penetrate only extremely thin sheets of materials such as the common



Figure 31. One of the main units for the production of plutonium at the massive plants located in southeastern Washington. (Courtesy of *The Atomic Energy Commission*.)

metals. Beta particles are more energetic (usually) and correspondingly more penetrating. These particles have velocities as great as 100,000 miles per second, and they can readily penetrate metal sheets one thirty-second of an inch in thickness. The extreme penetrating power of gamma rays attests their high energies and renders them an especial hazard; the more energetic gamma rays can penetrate almost unbelievable thicknesses of common materials of construction and, for example, blocks of lead one foot thick.

Because of the beta and gamma activity characteristic of several of the fission products associated with plutonium produced in the chain-reacting pile, all of the earlier stages in the chemical processing must be done by remote-control methods. That is, the vessels in which the

necessary chemical reactions are carried out are surrounded by walls of concrete "shielding" several feet thick, and the workmen must perform all operations without direct observation of the materials with which they are working. If this were not done, the chemical-plant personnel would suffer exposure to gamma radiation to an extent

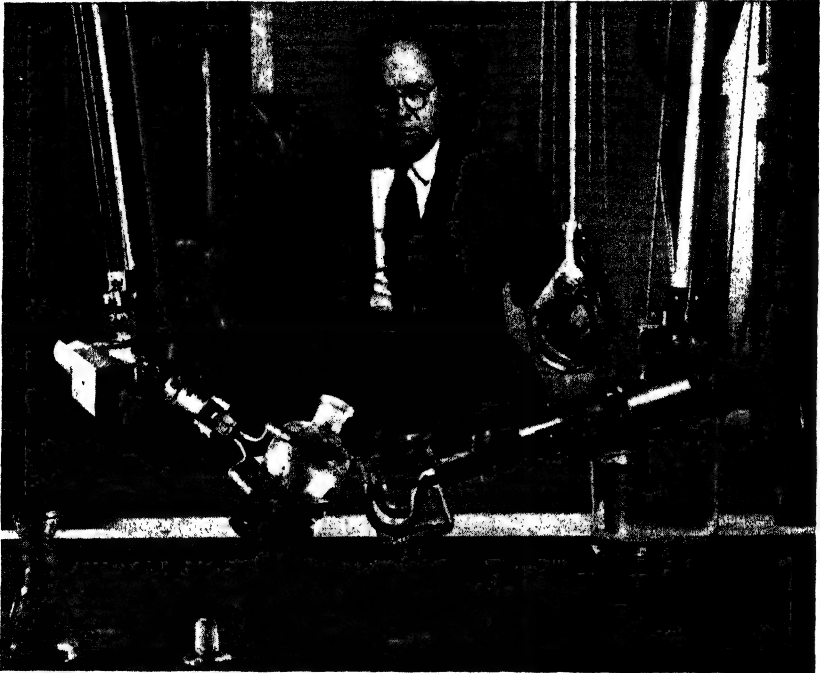


Figure 32. A remote-control manipulator designed by John Payne, of the General Electric Co. These "mechanical hands" extend over a protective wall into a radioactive area in which delicate experiments are performed by an operator who remains in an adjacent room. (*Courtesy of The General Electric Co.*)

that would quickly lead to fatal results. Somewhat the same sort of precautions are commonly necessary in laboratory work with radioactive materials, particularly those which emit gamma rays. Many ingenious remote-control devices have been invented for the purpose of permitting one to work with these substances and yet remain at a safe distance or behind an adequate shield (see Figs. 32 and 33).

Non-military Aspects of the Atomic-energy Problem. The rate of progress from the discovery of nuclear fission in 1939 to the dropping of

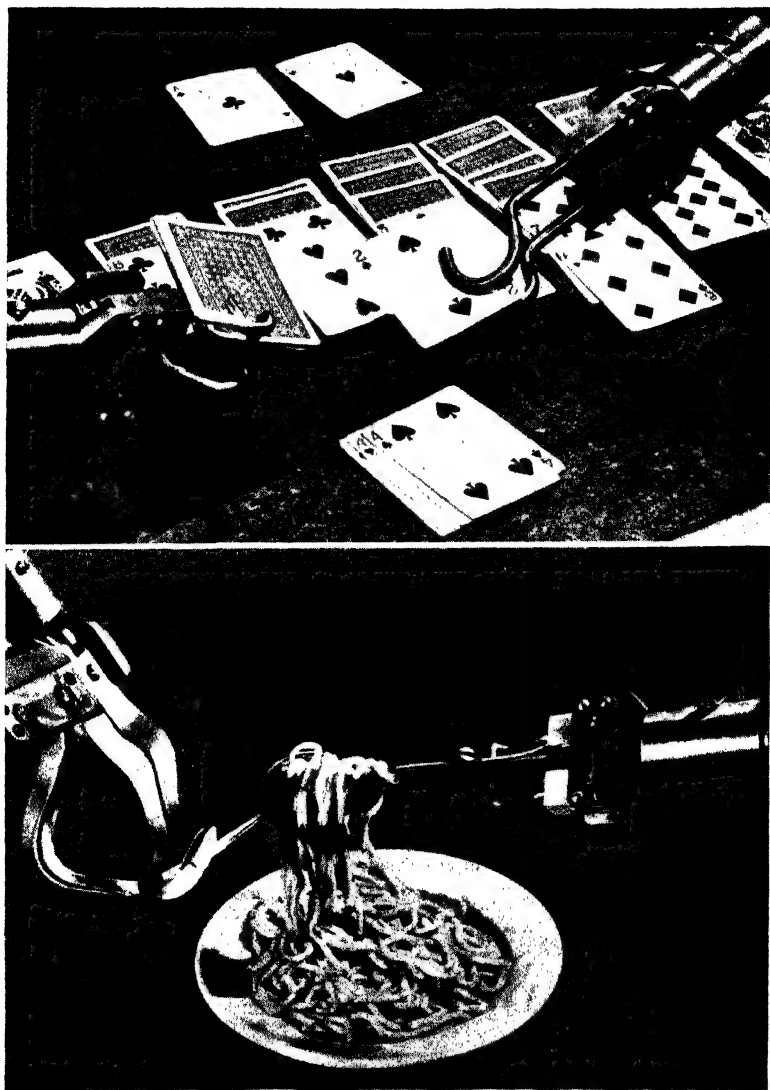


Figure 33. The dexterity of the remote-control manipulator shown in Figure 32 is illustrated above by two photographs showing its use to play a game of "absentee solitaire" and to twirl spaghetti on a spoon. (Courtesy of The General Electric Co.)

the first atomic bomb in 1945 is unprecedented in scientific history. There were several contributing factors. The general urgency of the war period and the fear that the enemy might achieve success first, coupled with a wealth of skilled technical man power, natural resources, and industrial "know-how," combined to accomplish in six years what otherwise might not have been brought to fruition in fifty years.

There is no wish here to become involved in arguments concerning the social, political, or moral aspects of these recent discoveries. It should, however, be emphasized that belated recriminations are certainly superfluous. If these discoveries had not been made when they were, the net result would have been nothing more than delay. The nature of scientific progress is such that these discoveries were inevitable, and there is no reason to believe that mankind would have been any more capable of solving the attendant humanitarian problems many years hence.

Rather, it is of prime importance that we realize that the benefits which will accrue from this new knowledge will greatly overshadow the purely destructive implications. Although it may not be anticipated that atomic power will quickly become competitive with conventional power sources for domestic or industrial use, the prospects for specialized uses are indeed bright. One must remember that nuclear science is truly in its infancy, that fissionable materials other than uranium and plutonium may come into use, and that great strides will be made in the direction of improved design of chain-reacting units and methods for the utilization of the energy which they provide. Experimental work done during World War II and subsequently shows clearly that chain-reacting power units of small size may be built and used. This suggests their use in submarines, ships, and other places wherein the still necessary heavy shielding materials can be accommodated. Economically, atomic power is and for a long time will be at a competitive disadvantage. This, however, does not preclude the possibility of using atomic power units in places remote from normal supplies of power, e.g., in the arctic regions.

Even though we discount entirely the practical non-military use of atomic power per se, there still remain some more important by-product gains. We have reference here to the new knowledge that has already resulted and will continue to result from studies employing the new or now more readily available isotopes of most of the elements. One dis-

^
tinct advantage inherent in the use of radioactive isotopes lies in the fact that they may be detected and measured by virtue of their radioactivity. Through the use of any of a number of different types of electronic instruments (the most common of which is the *Geiger counter*) it is possible actually to measure and record automatically the number of atoms that undergo decay in some suitable time interval. These measurements may be made more rapidly (although not necessarily more accurately) than through the use of conventional methods of chemical analysis.

Although one might cite literally hundreds of potential uses for radioactive isotopes, it is feasible to include only a few typical examples. Many of these applications involve the so-called "tracer" technique, in which a small quantity of a radioactive isotope is added to a large quantity of material containing the corresponding stable isotopes. Since both active and stable isotopes exhibit the same chemical behavior, one may detect what happens to the stable materials by following the behavior of the active isotopes that are so readily detectable by instrumental methods. Suppose, for example, that one wished to study the manner in which plants utilize phosphorus added to the soil in the form of a fertilizer consisting of the compound $\text{Ca}(\text{H}_2\text{PO}_4)_2$. A suitable approach would be to prepare some of this compound, using radioactive phosphorus (for example, $^{32}_{15}\text{P}$), and mix a little of this prepared "tracer" with the commercial fertilizer. One might apply the fertilizer to the soil at different depths or at different distances from the plant root system and thus determine the influence of these factors upon the rate of utilization of phosphorus by the plant. Optimum conditions for the most effective use of fertilizers might thus be established and waste avoided. Detection of the presence of phosphorus (*from the added fertilizer*) in the plant could be accomplished readily by taking samples of the plant tissue at regular intervals and determining whether they contain radioactive phosphorus and how much. Alternatively, one might wish to learn how phosphorus utilization depends upon the nature of the phosphorus-containing compound used or what happens to the phosphorus after it enters the plant. Studies of this sort frequently employ *radioautographs*, which are photographs made by taking advantage of the fact that particles and rays produced during radioactive decay affect the photographic plate in much the same manner as ordinary light rays. This amounts to

saying that objects containing interspersed radioactive atoms are capable of taking their own pictures; some typical examples are shown in Figs. 34, 35, and 36.

Through the use of similar methods a multitude of technical problems in many different fields of interest may be solved more readily than was possible by older techniques. Still other problems that could not be attacked at all successfully are now possible of solution because of the availability of radioactive isotopes and methods for their use. These new research tools are being used to determine what happens to drugs administered to the human body and how they function in the cure of diseases. As tracers, active isotopes will be used as aids in medical diagnosis; their radiations will be used in the treatment of disease. It seems highly probable that these techniques will contribute greatly to an ultimate understanding of the cause of cancer and the development of methods of treatment. Extensive studies in animal and plant metabolism, the role of vitamins, hormones, etc., in human nutrition, and a variety of related problems are already under intensive investigation.

We shall resist the temptation to dwell upon some of the more spectacular if not indeed fantastic applications that have been suggested for atomic power and radioactive isotopes. One additional fact, however, is worthy of special emphasis. Not by any means the least important application of radioactive isotopes is their use to determine how atoms behave during the course of chemical reactions. These studies together with scientific inquiry into the nature of the changes that go on in atomic nuclei will lead to a better understanding of

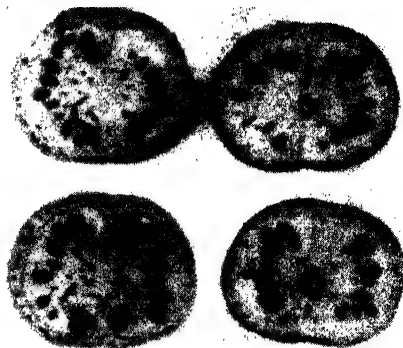


Figure 34. A radioautograph showing the distribution of radioactive zinc in tomatoes. The active isotope was administered to the plant in the form of zinc chloride. The black areas correspond to the location of the radioactive zinc and show that it concentrates primarily in the seeds of the tomato fruit. (*Courtesy of P. Stout and J. G. Hamilton, University of California.*)



Figure 35. (*Below*) An X-ray photograph of an amputated human leg showing the femur, tibia, and patella (kneecap) of a patient who had an osteogenic sarcoma (cancer of the bone). Prior to the amputation, radioactive strontium (Sr^{90}) was administered to the patient. (*Above*) A radioautograph, which shows the heavy deposition of radioactive strontium (black areas), particularly near the sarcoma. (Courtesy of C. Pecher and J. G. Hamilton, University of California.)

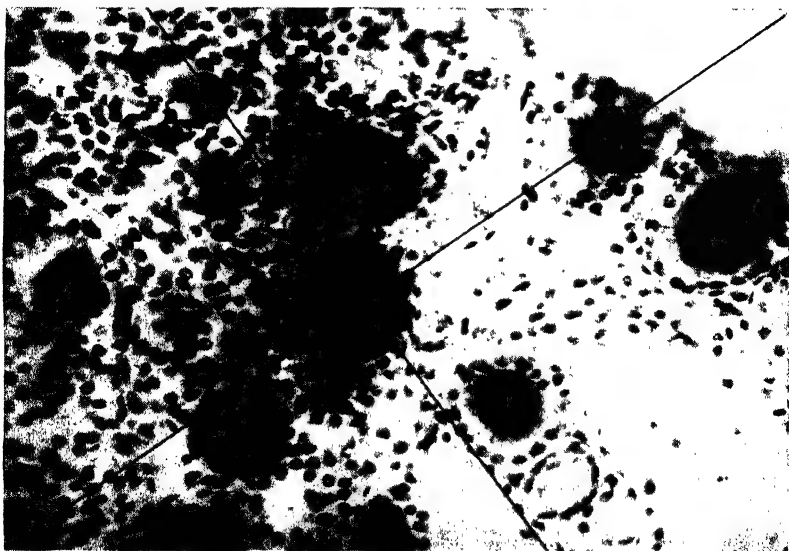


Figure 36. A radioautograph showing the localization of radioactive iodine (I^{131}) in the thyroid follicles of a rat. (Courtesy of George A. Boyd, The University of Rochester, School of Medicine and Dentistry.)

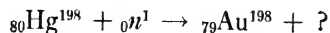
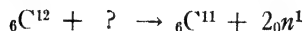
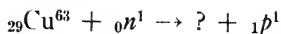
the constitution of matter and of mass-energy relations. Progress along these fundamental lines will have directly or indirectly a profound influence upon all phases of science and indeed upon all phases of human activity.

Studies concerned with uses of radioactive materials have come to be considered somewhat arbitrarily as constituting a branch of chemistry called *radiochemistry*. Although the distinction is by no means clear, studies relating to nuclear changes per se are commonly referred to as *nuclear chemistry* or *nuclear physics*.

EXERCISES

1. *New terms*: isotope, Geiger counter, half-life period, deuteron, radioautograph, betatron, chain-reacting pile, fission, mass number, positron, radiochemistry, decay series, nuclear chain reaction, cyclotron, heavy water, moderator, tracer, element.
2. Distinguish between atomic weight and mass number.
3. Compare the relative energies of alpha and beta particles and gamma rays.
4. Why must a pile be of a certain size before a self-sustaining chain reaction can occur in it?
5. Summarize the ways in which nuclear reactions differ from ordinary chemical reactions.
6. What property is possessed by the terminal member of any decay series?
7. In what respect are all isotopes of a given element the same?
8. Suggest a reason why self-propagating nuclear chain reactions do not occur in nature.
9. The first member of each of the known natural radioactive decay series is of very long half-life. Why must this be true?
10. How are electrons repelled when they are used in an effort to cause the occurrence of nuclear reactions?
11. In view of the existence of three isotopes of hydrogen, write formulas for all of the possible varieties of water in addition to H_2O and D_2O .
12. In carrying out nuclear reactions, why is the use of neutrons advantageous?

13. Draw diagrams representing the complete structures of atoms of the following pairs of isotopes: ${}_2\text{He}^3$ and ${}_2\text{He}^4$, ${}_{14}\text{Si}^{28}$ and ${}_{14}\text{Si}^{30}$, ${}_{16}\text{S}^{32}$ and ${}_{16}\text{S}^{36}$.
14. Complete the following equations by supplying the missing symbol together with its appropriate atomic number and mass number:



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The Atmosphere

SOME of the topics included in the preceding chapter have so captured the imagination that anything to follow may seem anticlimactic. At first glance, the study of the gaseous atmosphere in which we live may seem prosaic by comparison. On the other hand, some of these less spectacular aspects of the science of chemistry are none the less important. From a positive viewpoint one need only recognize that the atmosphere is necessary to all life processes and its peculiar characteristics determine the nature of the forms of life that may exist upon this or any other planet. Those who are more impressed by destructive forces may well consider the havoc wrought by atmospheric disturbances such as tornadoes, hurricanes, and the like. In any case, the atmosphere about us provides the most familiar avenue to the study of matter as it exists in the gaseous state. This is somewhat fortuitous since gases are comparatively simple forms of matter and consequently provide a gradual approach to the study of the more complex forms, *i.e.*, liquids and solids. In the consideration of this or any other scientific problem, it is axiomatic that a thorough study of the very simplest aspects usually provides information useful in the elucidation of the more complex features.

The Nature of the Atmosphere. The term *atmosphere* is normally used to denote the gaseous envelope that covers the entire surface of the earth. The portion of the atmosphere that is contiguous with the earth's surface is known as the *troposphere* and extends outward from the earth to a distance of some six miles. Of lesser interest in the present discussion is the outer atmosphere, or *stratosphere*, which extends beyond the troposphere to a distance that is both great and the subject of considerable disagreement. Although knowledge of the composition of the stratosphere is far from complete, it is known to contain at least some of the component elements of the troposphere. Because the

latter includes the portion of the atmosphere in which we live, it will be considered here to the exclusion of the stratosphere.

The early Greeks devoted considerable attention to the nature of the atmosphere, but they learned very little that was of lasting value. The material nature of "air" was clearly recognized several hundred years before the time of Christ and still later came to be looked upon as one of the elements (this was during the period when the concept of the term element embraced, for example, such things as the earth, air, water, and fire). It was not until the latter part of the eighteenth century that Cavendish and Scheele independently demonstrated that the atmosphere consists principally of the two gases nitrogen and oxygen. A clear understanding of the true nature of the atmosphere, however, was to await the experimental work of Bunsen, who showed that the air is a *mixture* having a variable composition.

Components of the Atmosphere. It is convenient to consider that the atmosphere is made up of (1) normal constituents and (2) accidental constituents, or "impurities."

If a sample of air were selected at random, dried to remove water, and analyzed, it is highly probable that the results would show that the sample contained 78 per cent nitrogen and 21 per cent oxygen. The remaining 1 per cent consists of the following elements and compounds (listed in order of *decreasing* abundance): argon (symbol A); carbon dioxide (formula CO_2); hydrogen; neon (symbol Ne); krypton (symbol Kr); helium (symbol He); ozone (formula O_3); and xenon (symbol Xe).

The fact that nitrogen and oxygen together comprise essentially 99 per cent of dry air and that these two elements are present in a very nearly constant ratio suggests the possibility that they may exist in the atmosphere in the form of a nitrogen-oxygen compound. One must conclude that such is not the case because the percentages of these two elements in dry air is not *exactly* constant, because they are not present in a ratio that corresponds to any probable formula for a compound of these two elements, and because the two gases may be separated by purely physical (mechanical) methods that involve no change in chemical composition. Air is thus a mixture of gases, but nevertheless a mixture that exhibits truly remarkable uniformity of composition. Precise chemical analyses show that minor variations in the composition of the atmosphere occur and that these depend upon latitude, the

nature of the vegetation, and other variations in particular conditions that prevail in different regions on the surface of the earth.

The presence of ozone in the atmosphere is attributable to the action of electrical discharges (lightning) upon the oxygen present therein. Although the average ozone content of the troposphere probably does not exceed one part in ten million parts of air, it is known to be present in greater amounts in the stratosphere. Were it not for the presence of ozone in the atmosphere, the forms of life that exist upon the earth might be quite different. This is because ozone removes (absorbs) from sunlight much of the ultraviolet radiation, which otherwise most certainly would have exerted profound influences upon the course of biological evolution.

The accidental components of the atmosphere owe their presence to the particular conditions that prevail over the earth's surface. These components include both organic and inorganic dust particles (*e.g.*, microorganisms, plant spores, salt from ocean spray), traces of nitrogen-oxygen compounds formed by electrical discharges during storms, ammonia (NH_3) produced during the decay of animal and vegetable matter, etc. The presence of dust particles in the atmosphere is a matter of no little importance. Some of these particles include molds and bacteria that settle to the earth and cause putrefaction of organic matter and lead to a number of different diseases. Dust particles give rise to clouds, fog, and rain; *i.e.*, they serve as centers for the condensation of atmospheric moisture, and thus fog and finally raindrops are formed. If the air were entirely free of these dust particles, there would be no market for umbrellas because moisture would condense uniformly upon all surfaces and would not fall as raindrops. The blue color of the sky is due to the reflection and scattering of light rays by these particles (including the gas molecules).

In regions of high population density and/or a high level of industrial activity, more or less localized gaseous impurities commonly present in the atmosphere include the element chlorine (Cl_2), the compounds hydrogen sulfide (H_2S), sulfur dioxide (SO_2), carbon dioxide (CO_2), carbon monoxide (CO), etc. In any event, the quantities of these impurities are usually too small to detect by other than the most sensitive methods of analysis.

The atmosphere is the most familiar example of the existence of matter in the gaseous state. A better understanding of the real character

of the atmosphere may accrue through a study of those properties which typify matter in this particular physical state.

The Nature of Matter in the Gaseous State. It is entirely appropriate that, of the three states of matter, gases should be studied first. They are simpler in their make-up, exhibit much greater uniformity in physical properties, and consequently do not involve many of the complications that are encountered in the study of liquids and solids.

The Scientific Method. With the exception of those few common gases that possess characteristic colors or odors, gases are truly unobtrusive. Our every motion or act is influenced by the gaseous medium about us, and yet we give scant thought to its existence. If one collides with a solid object, the impression thereby created is profound; but we continually collide with gas molecules and are none the worse for the experience. On the other hand, much may be learned about the nature of gases by some reasonably simple experiments. Suppose, for example, that we select two highly odoriferous gases and release them in still air in one corner of a closed room. Rather quickly their typical odors will be detectable at the opposite corner of the room, and—if the gases are properly selected—one will be detectable more quickly than the other. One may reason (1) that the gas molecules moved through space (and quite rapidly) and (2) that the one kind of gas molecule moved more rapidly than the other. Taken all together, such singularly simple observations plus the results of somewhat more elaborate experiments provide a body of information that has accumulated over a period of many years. When sufficient *experimental* information became available, scientists found it possible to piece together the various experimentally demonstrated facts about gases and thus began to arrive at an understanding of their constitution. The collection of the requisite experimental data and observations constitutes the first step in the so-called *experimental method*, or *scientific method*. The second stage is the utilization of these facts in arriving at an understanding of the materials under study. This may evolve via a *hypothesis*, which is a proposed explanation comprising nothing more than an intelligent guess that may actually have little basis in experimental fact. More typically, one uses the experimental evidence to formulate a *theory*, *i.e.*, a reasonable explanation of the experimentally observed facts. The third step in the scientific method is the devising of further experiments which will put the theory to such rigorous tests that the theory will be

either substantiated or disproved. Theories that withstand the test of time and are not negated by new information usually come to assume the status of scientific laws. Throughout all science, the term law implies a statement that *describes* natural phenomena and is not to be confused with its connotation in jurisprudence. Laws made by legislative action are designed to *regulate*; the laws of science merely *describe* natural phenomena.

The Kinetic-molecular Theory. With reference to gaseous matter, what we need is a mental picture or theory that will enable us to understand the constitution of these material substances, many of which are invisible, odorless, tasteless, and otherwise unimpressive. The theory should enable us to explain the results of experiments and to predict the results to be anticipated from experiments as yet untried. Such is the kinetic-molecular theory—the theory of molecules in motion.

In terms of this firmly established set of ideas, gases are considered to consist of individual gas molecules that are separated by much unoccupied space. That is, the distance between gas molecules is very great in comparison with the diameters of the individual molecules. (If the reverse were true, gas molecules packed close together would represent a form of matter so dense that we should encounter great resistance in walking through a gaseous atmosphere.) The theory holds further that gas molecules at ordinary temperatures are in a state of wholly unordered motion through space. A molecule moves in one direction until it collides with another molecule, whereupon they rebound without loss of energy, *i.e.*, they rebound at velocities the same as they had before the collisions occurred. (If this were not the case, gas molecules would steadily lose energy owing to successive collisions, they would “run down,” so to speak, and molecular motion would cease.) The kinetic energy¹ possessed by gas molecules depends upon the temperature and is greater the higher the temperature. An item of major importance in the theory is the fact that, at any given temperature, *the average kinetic energy of all different kinds of gas molecules is substantially the same*. This does not mean that all molecules under a given set of conditions have *identical* kinetic energies; some have greater and some have less than the average value. Still another feature of the kinetic-molecular theory is one of relatively lesser im-

¹ Kinetic energy is the form of energy possessed by moving bodies by virtue of their motion.

portance for present purposes. This has to do with the existence of a force of attraction between gas molecules—a force which becomes significant only near the temperature at which the gas changes to a liquid.

If it may now be admitted that this collection of ideas about the nature of gases could not have arisen without at least some foundation in experimental fact, we come to the most critical feature of this or any other theory. How well does the theory enable us to explain our day-to-day observations? From the discussions which follow it should become evident that the kinetic-molecular theory enables us not only to explain what gases do under one set of conditions but also to predict how they will behave under other sets of conditions. In succeeding chapters, it will be shown how this theory may be extended to liquids and solids.

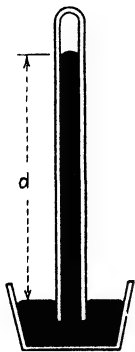


Figure 37.
A simple barometer.

Atmospheric Pressure. Wholly consistent with the kinetic-molecular theory is the fact that we encounter only little resistance owing to collisions with gas molecules as we move from place to place. Gases must truly consist of molecules separated by otherwise empty space.

The force exerted upon us by the gas molecules of the atmosphere is none the less real. As gas molecules move erratically through space, they collide with all exposed surfaces and these billions of impacts constitute the *pressure* exerted by all gases, atmospheric or otherwise.

The reality of the pressure exerted by the atmosphere was first clearly demonstrated in 1643 by the Italian scientist Torricelli, who was a student of Galileo. Torricelli sealed one end of a long glass tube, filled it with mercury, placed his thumb over the open end, inverted the tube, and immersed the open end under the surface of mercury in another vessel before removing his thumb. The result is illustrated by Fig. 37. The level of the liquid mercury in the tube dropped, but only to a fixed point in the tube. The fact that the mercury did not drop in the tube until the two liquid levels were equal means that the column of mercury remaining in the tube must be supported by an outside force. This force necessarily must be the pressure due to the atmosphere, *i.e.*, that exerted by virtue of impacts of atmospheric gas molecules upon the surface of the mercury in the bottom vessel.

The simple arrangement shown in Fig. 37 is the most rudimentary form of *barometer*. The magnitude of the pressure exerted by the atmosphere is measured by the distance d between the two liquid levels. At sea level, the atmospheric pressure is sufficient to support a column of mercury 76 cm. (760 mm.) in height; thus $d = 76$ cm., or approximately 30 inches. A *barometric pressure* amounting to 760 mm. is commonly called a pressure of *one atmosphere*.

Still another characteristic of the atmosphere warrants mention here because of its practical importance. Upon examination of the character of the atmosphere in relation to progressively greater and greater distance from the earth's surface, it is found that the atmosphere becomes progressively less dense—*i.e.*, there are fewer and fewer molecules and more and more empty space. Because there are fewer gas molecules, they collide less frequently (assuming that there is no change in temperature) and consequently exert less pressure. If one should repeat Torricelli's experiment at the top of a mountain 12,000 feet above sea level, for example, one would find that the pressure would be considerably less than 760 mm. A further consequence of this lower pressure at high altitudes will be encountered in the following pages. Since the total number of gas molecules per unit of volume is less at high altitudes, it follows that there are fewer *oxygen molecules*—hence the physiological effects (resulting from limited oxygen supply) that most of us experience at high altitudes, and the need for a supplementary oxygen supply in aircraft operated at high altitudes.

Finally, with reference to Fig. 37, it should be noted that the space above the column of mercury in the tube can contain nothing but the extremely small number of mercury atoms which can exist in the gaseous state at ordinary temperatures. This space is therefore a *vacuum* and for obvious reasons is still referred to as a Torricelli vacuum.

Dalton's Law. In order to explore another aspect of the behavior of gases, let us assume that in the atmosphere about us all of the oxygen has been replaced with nitrogen so that the atmosphere now consists of pure nitrogen. Under these conditions, what pressure would this nitrogen atmosphere exert, for example, at sea level? Would it be greater, less, or equal to 760 mm.? The answer to these questions is based upon observations first clearly interpreted by John Dalton and falls within the scope of the law that still bears his name. Actually, one would

find that the pressure exerted by a pure nitrogen atmosphere at sea level would be exactly the same as that of the normal atmosphere, and this statement may be verified by very simple laboratory experiments. In other words, the exertion of pressure by a mixture containing a certain total number of gas molecules does not differ from the exertion of pressure by the same number of molecules of a pure gas at the same temperature. This finding, again, is entirely consistent with expectations based upon the kinetic-molecular theory. Most simply stated, Dalton's law merely holds that *the total pressure exerted by a mixture of gases is the sum of the pressures exerted by the individual gases in the mixture*. If, in a given container, we have gases *A* and *B*, the total pressure is that resulting from *A* plus that due to *B* and the respective contribution of each gas is known as its *partial pressure*. With respect to the exertion of pressure, each gas behaves independently—entirely uninfluenced by whatever other gases may be present.

Henry's Law. The gases that make up the atmosphere exert pressure upon all objects regardless of their physical state. Thus, at sea level, gas molecules strike the surface of oceanic waters, and some of these gas molecules enter (dissolve in) the water. At any given temperature, the number of gas molecules that will dissolve in a specified volume of a liquid such as water is clearly dependent upon the number of collisions of gas molecules with the surface of the liquid. On the surface of a mountain lake there will be relatively fewer impacts and correspondingly fewer molecules dissolved. Accordingly, the oxygen supply in the waters of a mountain lake must be less than in lake water near sea level. This must undoubtedly influence marine life, but this idea will not be pursued further lest it become involved in the relative merits of trout fishing versus deep-sea fishing. More to the point is the inescapable conclusion relating to the influence of gas pressure upon the extent to which gases dissolve in liquids and known as Henry's law: *At any specified temperature, the extent to which a gas dissolves in a liquid is directly dependent upon the gas pressure.*

Ordinary soda water consists of carbon dioxide gas dissolved in water under a rather considerable pressure. When the cap is removed, the sudden release of pressure permits the escape of gas molecules and this is exactly the result to be expected to accompany the attendant decrease from a high pressure to the relatively much lower atmospheric pressure.

The Water Content of the Atmosphere. A component part of the atmosphere that has much bearing upon our everyday comfort is gaseous water, or *water vapor*. The water content of the atmosphere is quite variable and is usually expressed in terms of *relative humidity*. At any prevailing temperature, the quantity of water vapor that can exist in the atmosphere is limited and increases with increase in the temperature. When, at a given temperature, the atmosphere contains the maximum possible quantity of water vapor, the atmosphere is said to be *saturated* and the humidity is considered to be 100 per cent. If the air contains, for example, only one-half the quantity of water vapor possible at that temperature, the relative humidity is 50 per cent, etc.

Our personal comfort depends upon a favorable balance between the water content of the atmosphere and the temperature. In any geographical region where a set of conditions conducive to comfort prevails, the residents boast about the climate; where just the reverse is true, the inhabitants describe the weather as "unusual." The normal temperature of the human body is 98.6° on the Fahrenheit temperature scale,¹ and any appreciable deviation from this value occasions discomfort. The chief regulatory mechanism is the evaporation of water from the surface of the body, and this is in turn dependent upon the quantity of water already in the atmosphere. If the relative humidity is near 100 per cent, it is obvious that evaporation is not favored and we thus experience oppressively "humid weather." The metabolic and other processes that go on in the body are of such nature that they liberate heat, and this heat must be continuously dissipated either by radiation or as a result of evaporation of water if the normal body temperature is to be maintained. At this temperature (98.6°F.), nearly 600 calories of heat is required to evaporate one gram of water. From this fact it may be estimated that the evaporation of as little as 0.35 oz. of water from an average-weight human body will lower the temperature approximately 0.25°F. Consequently, low relative humidity is essential to comfort, but still other factors are involved. As moisture evaporates into still air, the air immediately surrounding the body undergoes an increase in relative humidity and may indeed become saturated with water vapor. A natural movement of the air or one created by a fan therefore produces a cooling effect simply because the

¹ See Chapter 8.

more humid air at the body surface is swept away and replaced by air having a lower water content, thus permitting further evaporative cooling.

Seasonal variations in relative humidity are particularly important in connection with the maintenance of a comfortable and healthful atmosphere in the home. In cold weather, when houses are tightly

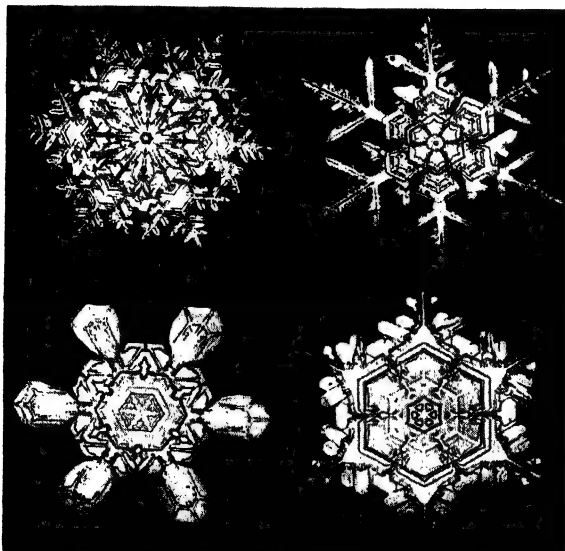


Figure 38. Snow crystals. (*Courtesy of the American Museum of Natural History.*)

closed, the water content of the outside atmosphere is lower than during any other season. When this air is heated to a desirable temperature inside the house, the water content of the air is no longer in correspondence with the temperature, *i.e.*, the relative humidity is too low. It is for this reason that it becomes important to add water vapor by providing a reservoir of water near the source of the heat. Essentially the reverse situation prevails during the hot summer months in those regions which are characterized by high humidity, but the remedy is by no means so simple.

Finally, it should be recognized that what we experience in the way of "weather" is largely dependent upon the existing relation between temperature and the water content of the atmosphere. When moist air is cooled sufficiently, there is reached a temperature at which the prevailing water content exceeds 100 per cent humidity. Thereupon, water

vapor changes to very tiny droplets of liquid water that condense upon dust particles and appear in the form of fog or clouds. If the quantity of water that separates is sufficient, these tiny drops coalesce, form larger drops, and fall as rain. When, in their passage through the atmosphere, these drops fall through a region of very low temperature, they freeze and fall to the earth as hailstones. If, on the other hand, the separation of water occurs initially at a temperature below that at which water freezes (32° on the Fahrenheit temperature scale), ice forms in characteristic hexagonal crystals (Fig. 38) and falls to the earth in the form of snow.

From this admittedly incomplete account, it should be clear that what takes place in the atmosphere about us is a matter of no little interest to all of us.

The Inert Gases. Thus far, several normal constituents of the atmosphere have not been singled out for special consideration. Six of these, namely, the elements helium, neon, argon, krypton, xenon, and radon, constitute a family of elements called the inert gases, and it is convenient to consider them together since they exhibit such striking similarity in their lack of chemical properties.

Occurrence. The discovery of the element argon arose in a manner that typifies many scientific discoveries. The Englishman, Lord Rayleigh, found the essential clue in some fairly simple experiments. He weighed a certain volume of nitrogen gas that was known to be of very high purity and found the weight to be 1.2505 g. He then weighed exactly the same volume of nitrogen obtained from dry air by removing all of the oxygen and found in this case a weight of 1.2572 g. Since, at that time, dry air was thought to contain only nitrogen and oxygen, Rayleigh's results suggested that the presumably pure nitrogen from the air must actually contain one or more impurities *heavier than nitrogen*. In 1894, Rayleigh, together with Sir William Ramsay, proceeded to examine samples of dry air with a view to determining the identity of this unknown impurity. From samples of dry air, they first removed the oxygen, then the nitrogen, and in every case there remained a volume of gas amounting to about 1 per cent of the original sample of dry air used in the experiment. Because they were unable to devise any set of conditions under which this gas would combine with any other element, they decided that the gas must be a new element and gave it the name argon (from the Greek word meaning *lazy*,

or *inactive*). They were soon to find, however, that although this gas consisted principally of argon it contained also small quantities of other inert gases; these are neon (Greek, *new*), krypton (Greek, *hidden*), and xenon (Greek, *stranger*). The inert gas helium (Greek, *sun*) occurs in very small quantities in the earth's atmosphere, but this element was known to be present in the atmosphere of the sun as early as 1868.

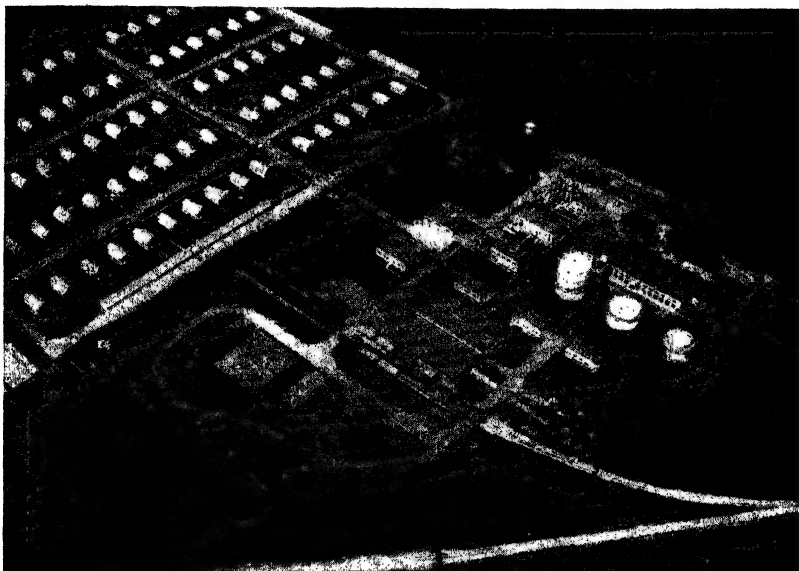


Figure 39. Aerial view of the world's largest plant for the production of helium. This plant is located at Excell, Tex., about forty miles north of Amarillo. (Courtesy of the Bureau of Mines, United States Department of the Interior.)

This gas is also found trapped in numerous minerals and ores, particularly those of uranium, where its existence is attributable to its formation as a product of the radioactive decay of elements that emit alpha particles. Probably of the same origin is the helium produced from many natural gas wells, particularly those in Kansas and Texas (Fig. 39). The heaviest of the inert gases, radon, is also a product of radioactive decay and occurs in the atmosphere to an extent that is small but nevertheless measurable.

Properties. The inert gases are unique among the chemical elements in that they do not enter into chemical reactions; their atoms do not lose, gain, or share electrons. Earlier statements relative to the sta-

bility of the electronic structures of the atoms of the inert gases (Chapter 5) are entirely consistent with the experimental facts. So stable are these structures that these gases do not even combine with themselves to form simple diatomic molecules as do the common gases such as H_2 , O_2 , and N_2 . Thus, the inert gases occur as single atoms and are therefore represented simply by their symbols.

Because of differences in their atomic masses, the inert gases do exhibit appreciable differences in physical properties. These differences provide the only basis for the separation of the inert gases from each other.

Uses. From the standpoint of large-scale production and use, helium is by far the most important of the inert gases. The chief use of helium is in the inflation of balloons, dirigibles, and other lighter-than-air craft. Although its "lifting power" is not so great as that of hydrogen (formerly used for such purposes), it possesses the great advantage of non-flammability. Helium is used also to inflate the tires used on airplanes; this application of course depends upon the fact that helium is so much lighter than air. Most of the world's commercial supply of helium is produced in the United States, and this country exercises rigid controls to prevent helium from becoming available for the military use of potential enemy countries. Helium is commonly mixed with oxygen used in therapy and in recent years has largely displaced nitrogen for use in decompression chambers in which deep-sea divers and workmen employed in deep underground tunneling operations are treated to prevent the "bends." Helium (and neon and argon as well) is frequently employed in scientific laboratories as a replacement for air when it is desired to conduct experiments in a chemically inert atmosphere. A recently developed and improved technique for the welding of active metals such as magnesium and aluminum employs an arc blanketed with helium gas (Fig. 40); argon is employed similarly.

The major practical application of neon is its use in airplane beacons, "neon signs," and the like. This application is based upon the fact that the passage of an electric discharge through neon (at low pressures) produces a characteristic and very penetrating orange-red glow. During travel by air over towns and cities one is particularly impressed by the extent to which this form of illumination has come to be used in advertising and with the fog-penetrating qualities of the light so produced. In addition to low cost, this form of illumination is advanta-

geous in advertising because of the striking variety of colors that may be employed, together with the intricate designs made possible by the use of tubing. The different colors are produced by the use of mixtures containing neon together with argon, helium, mercury vapor, traces of certain organic compounds, colored glass tubes, etc.

For many years, argon has been used in place of nitrogen in electric-light bulbs. Advantages inherent in the use of argon include longer use-



Figure 40. Helium is used to provide an inert atmosphere in new methods for the welding of metals such as magnesium and aluminum. (*Courtesy of the Bureau of Mines, United States Department of the Interior.*)

ful life, higher efficiency, and a light more nearly comparable to natural daylight. Because they are less abundant and more difficult and costly to produce, krypton and xenon have been little used. It has been known for a long time that krypton is even better than argon for use in lights, but only in very recent times has krypton come into use for this purpose. The thirty-five krypton flash approach lights now in use at the New York International ("Idlewild") Airport are reputed to be the brightest lights ever made by man and to have a surface brightness (per square inch) ten times greater than that of the sun. A particular virtue of krypton lamps for use at air terminals and in route beacons is their unusual capacity to penetrate extremely dense fog.

There is experimental evidence also to indicate that xenon will soon

find extensive application in the manufacture of multi-element radio tubes, cathode-ray tubes for television sets, and other similar uses in electronics.

The Atmosphere as a Source of Raw Materials. Although one is accustomed to think of the raw materials for industry as coming primarily from deposits on or within the earth's surface, *e.g.*, iron ore, coal, petroleum, limestone, salt, etc., the gaseous atmosphere also plays an important role. Of course, air is the source of neon, argon, and krypton used commercially. Of greater importance however are the nitrogen and oxygen that annually are extracted (directly or indirectly) in thousands of tons and used for many different purposes. In connection with subsequent discussions of industrial chemical processes, it is suggested that the student note how commonly one or more of the raw materials are provided by the atmosphere. Other noteworthy features of the atmosphere as a source of raw materials for industry are the essentially unlimited supply of air and the fact that up to the present time no means have been found to subject it to taxation.

EXERCISES

1. *New terms:* atmosphere, partial pressure, theory, relative humidity, troposphere, pressure, kinetic energy, barometer, law, water vapor, stratosphere, hypothesis, barometric pressure, Torricelli vacuum, one atmosphere.
2. *Laws:* Dalton's law, Henry's law.
3. Explain why dust particles are desirable components of the atmosphere.
4. Distinguish between (*a*) normal and accidental components of the atmosphere and (*b*) the troposphere and the stratosphere.
5. What are the three essential steps in the scientific method?
6. Give the approximate percentage composition of the troposphere.
7. Cite three reasons why it must be true that nitrogen and oxygen exist in the air as a mixture.
8. How may one account for the presence of ozone in the atmosphere? Why is its presence of importance?
9. Summarize briefly the essential ideas embodied in the kinetic-molecular theory.

10. What is the purpose of any theory?
11. How may a theory or a hypothesis come to be looked upon as a scientific law?
12. Draw a diagram representing a simple form of barometer.
13. What kinds of methods are used to separate the inert gases? Why must such methods be employed?
14. List the natural sources of the various inert gases.
15. Suggest an alternative explanation of the results found by Rayleigh in his comparison of the weights of the two different samples of nitrogen.
16. List the various practical applications for the inert gases.
17. Is the temperature of a room increased, decreased, or unchanged when an electric fan is put in operation? Explain.
18. A vessel contains hydrogen at a partial pressure of 100 mm., oxygen at a partial pressure of 150 mm., and nitrogen. If the total pressure is 500 mm., what is the partial pressure of nitrogen?
19. If the temperature of the atmosphere is 80°F. and the relative humidity is 65 per cent and the temperature rises to 90°, is the *relative* humidity equal to, greater than, or less than 65 per cent. Why?

COLLATERAL READING

- HATCHER: "An Introduction to Chemical Science," John Wiley & Sons, Inc., New York, 1940, Chapter V.
- HOLMES: "Introductory College Chemistry," The Macmillan Company, New York, 1946, Chapter XXVIII.
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Properties of Matter in the Gaseous State

IN PRACTICALLY every area of scientific knowledge, *classification* may be looked upon as a necessary evil. The disadvantage arises because the segregation and compartmentalization inherent in all schemes of classification tend to set up artificial barriers in our thinking. We classify matter according to physical state on the basis of differences in the properties of gases, liquids, and solids, and the initial emphasis upon these differences is likely to obscure the similarities that these forms of matter exhibit. It is essential, therefore, that the student come to realize that the apparent differences between the three states of matter are largely differences in degree, not in kind. Thus far, the kinetic-molecular theory has been applied only in a most elementary fashion. By keeping in mind the thought that this is the theory of *molecules in motion*, the close interrelationship of gases, liquids, and solids will become more readily apparent.

Everyone knows a good deal about gases even though unaware of the possession of such knowledge and unaccustomed to expressing the information in technical terms. A specific example already cited is the detection of the movement (diffusion) of gas molecules by odor. Observation of what happens when one inflates an automobile inner tube shows that gases may be compressed. Similarly the changes in pressure in the tube that all have noted when there are marked changes in temperature also reflect the influence of temperature upon the pressure exerted by gases. As will be the case also for liquids and solids, it shall be the purpose here to interpret the properties of gases in terms of the kinetic-molecular theory.

Units of Measurement. The ever-present requirement of exactness

in the expression of quantities necessitates some additional consideration of the units of measurement that are employed in chemistry and other exact sciences. Of all the various modes of expression of quantities, the metric system is that most commonly employed in scientific work.

Length. In the metric system, the unit of length is the *meter* (m.), which is equal to 3.2808 feet. Most often, lengths are expressed in fractions of a meter; the common fractional units are

The *centimeter* (cm.): $100 \text{ cm.} = 1 \text{ m.}$

The *millimeter* (mm.): $10 \text{ mm.} = 1 \text{ cm.}$

It is convenient to remember that one inch is equal to 2.54 cm.

Volume. The unit of volume is the *liter* (l.); this is a volume just a little larger than the quart, that is, $1 \text{ liter} = 1.0567 \text{ quart}$. Those who have traveled extensively may have already encountered this unit of volume in connection with the purchase of gasoline in Mexico or beer in Germany. Smaller volumes are usually expressed in terms of the *milliliter* (ml.), which is the one-thousandth part of a liter; thus $1 \text{ liter} = 1000 \text{ ml.}$ A similar unit, the *cubic centimeter* (cc.), is the volume enclosed by a cube 1 cm. on the inside edge. The difference between the cubic centimeter and the milliliter is so small that for most purposes the two units may be used interchangeably: $1 \text{ ml.} = 1.000028 \text{ cc.}$

Temperature. With only infrequent exceptions, temperatures are measured by the use of a *thermometer*. This is simply a long heavy-walled glass tube of small bore with a bulb at the lower end. The bulb is filled with a liquid (mercury, alcohol, toluene, etc.) which expands when heated and rises in the tube. The tube is marked with a graduated scale consisting of markings spaced at regular intervals. The reference points are arbitrarily taken as the temperature at which water boils and that at which ice melts. In industry and in the home (in English-speaking countries) the Fahrenheit scale is most often used; the centigrade scale is used almost exclusively in scientific work. It is said that Fahrenheit attempted to choose reproducible reference points for his temperature scale. He chose as 0° the lowest temperature that he could attain with a mixture of snow and salt. The temperature chosen as 100° was that of Fahrenheit's cow, but it turned out that the

cow was ill at the time, with the result that normal body temperature is 98.6° instead of the intended 100° . The relation between these two temperature scales is shown by Fig. 41. Because the divisions on the Fahrenheit scale are five-ninths as long as those on the centigrade, conversion of temperatures from the one scale to the other is done by means of the equations

$$^{\circ}\text{C.} = \frac{5}{9}(^{\circ}\text{F.} + 40) - 40$$

$$^{\circ}\text{F.} = \frac{9}{5}(^{\circ}\text{C.} + 40) - 40$$

Both these temperature scales are ones arbitrarily devised for reasons of convenience. A temperature scale having a more fundamental basis will be discussed later.

In scientific writings one finds frequent reference to *room temperature*. This typically denotes 25°C. , or 77°F.

Density. The term density carries the idea of compactness. Density is a characteristic property of matter in all three of the physical states. If a body of matter consists of particles packed very close together and thus has little empty space between particles, the material is said to be dense. Specifically, density is the weight or mass of matter contained in some appropriate unit of volume, *e.g.*, grams per liter, grams per cubic centimeter.

Densities of gases are usually expressed in grams per liter. Since the density of a gas is dependent upon both temperature and pressure, a value for density has no meaning unless both temperature and pressure are specified. The densities of a few common gases are listed in Table 2.

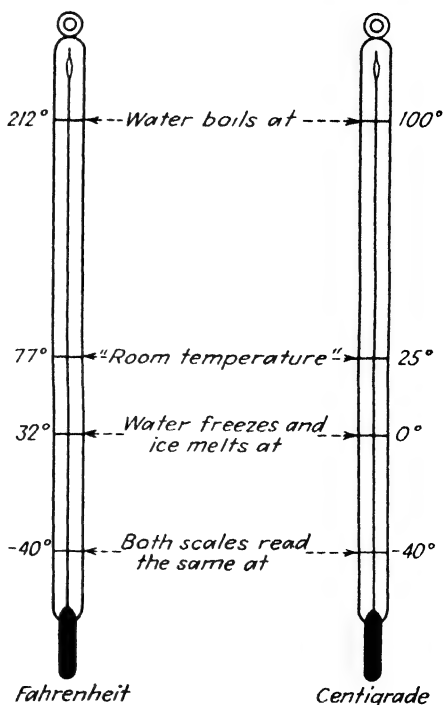


Figure 41. A comparison of the Fahrenheit and centigrade temperature scales.

TABLE 2. Density of Common Gases at 0°C. and a Pressure of One Atmosphere

<i>Gas</i>	<i>Density, grams per liter</i>
Hydrogen	0.0899
Helium	0.1785
Ammonia	0.7710
Nitrogen	1.2505
Air	1.2930
Oxygen	1.4290
Hydrogen chloride.....	1.6392
Sulfur dioxide.....	2.9269

Density Relative to Air. At times it is convenient to know whether a gas is heavier or lighter than air. For example, suppose that we plan to operate a large chemical-manufacturing plant in which one of the by-products is a toxic gas. If this gas is lighter than air, it will rise into the atmosphere and thus its potentially hazardous effects upon the immediate neighborhood would be eliminated or at least minimized. Similarly, laboratory procedures for the handling of gases are influenced depending upon whether the gas is heavier or lighter than air. Thus we may need to know the density in comparison with that of air, *i.e.*, the *relative density*. This is simply the density of the gas in question divided by the density of air. In Table 3 are listed the calculated values for the relative densities of the gases included in Table 2. Hydrogen, helium, ammonia, and nitrogen are lighter than air; oxygen, hydrogen chloride and sulfur dioxide are heavier.

TABLE 3. Relative Density of Common Gases at 0°C. and a Pressure of One Atmosphere

<i>Gas</i>	<i>Relative density</i>
Hydrogen	0.0696
Helium	0.1381
Ammonia	0.5963
Nitrogen	0.9671
Air	1.0000
Oxygen	1.1053
Hydrogen chloride.....	1.2677
Sulfur dioxide.....	2.2130

A clear distinction should be made between density and *specific gravity*. The latter is the ratio of the weight of any given volume of any substance to the weight of an equal volume of *water* at the same temperature.

For reasons that will be more evident upon further study of the application of the kinetic theory to liquids and solids, the densities of matter in these physical states are dependent upon temperature but relatively little dependent upon pressure. Substances capable of existence in either the liquid or the solid state are typically more dense when in the solid condition. An interesting exception is ordinary water, which is less dense in the solid state and exhibits its maximum density at a temperature of 4°C .¹ The lesser density of solid water is responsible for the fact that ice floats upon water. A little thought will show that if the reverse were true it would lead to some profound changes in the world about us.

The Influence of Temperature upon the Volume Occupied by a Gas. According to the kinetic-molecular theory the motion of gas molecules depends upon their kinetic energy. If the kinetic energy of gas molecules confined in a closed vessel should be increased by supplying additional energy in the form of heat (*i.e.*, if the temperature of the gas were raised), they would move more rapidly, collide more often, and consequently exert greater pressure upon the walls of the container. An automobile-tire "blow-out" is often the direct result of this sort of effect. If the tire is inflated to its optimum pressure on a cool morning, then driven over a hot highway surface, the resultant increase in pressure is often sufficient to rupture the inner tube and tire. Thus, when they are heated, gases *expand*—they tend to occupy greater volumes or to exert greater pressure if the volume cannot change. Conversely, if gases are cooled (kinetic energy decreased), they *contract* and tend to occupy smaller volumes or to exert lesser pressure in the same volume.

It is not sufficient just to know that the volume occupied by a gas changes when the temperature is changed. The important point is, *how much* change in volume results from a specified change in temperature? Let it be assumed that we want to study this problem and that we shall start with a sample of gas which occupies a volume of 273 cc. at 0°C . and a pressure of one atmosphere. Since the volume is influenced also by the pressure, one must use an arrangement of apparatus such that the pressure will remain constant at one atmosphere. In this way

¹ The temperature of maximum density of water is an important reference point in the metric system. The *gram* is defined as the weight of one cubic centimeter of water at 4°C .

it will be known that any observed change in volume will be due solely to the change in temperature. If, now, the temperature is lowered from 0 to -1°C , the gas is found to contract to a volume of 272 cc.; at -2° the volume is 271 cc. That is, for each one degree of lowering in the centigrade temperature, the volume of the gas decreases by one cubic centimeter. If the temperature could be lowered to -273°C ., it would appear that the gas should occupy zero volume. This obviously does not and cannot happen; such an occurrence would imply a complete disappearance of the sample of matter under investigation. Long before any temperature such as -273°C . were reached, the gas would first condense to a liquid, then freeze to a solid.

The temperature of -273°C . is nevertheless one of great significance even though it has never been achieved. It is, theoretically, the temperature at which molecular motion would cease; this temperature is specified as zero on the *absolute temperature scale*. Accordingly, to convert from centigrade to absolute temperatures, one need only add 273 to the former; for example, $25^{\circ}\text{C} + 273 = 298^{\circ}\text{A}$. By some very ingenious experiments, scientists have produced temperatures very near the absolute zero, that is, -272.996°C . (0.004°A .), and various forms of matter exhibit some quite unusual properties at these very low temperatures.

The regular decrease in volume with decrease in temperature (or increase in volume with increase in temperature) previously referred to would be found no matter which of the common gases were used in the experiment. It is a behavior that is characteristic of matter in the gaseous state. This regularity may be described by stating that *the volume occupied by a definite weight of a gas at constant pressure is directly proportional to the absolute temperature*. This is merely a statement of *Charles' law*, which was first enunciated in 1801.

Charles' law is indeed a convenient generalization that can save one much work. Suppose, for example, that we have a 50-cc. sample of gas at one atmosphere pressure and at a temperature of 25°C . (298°A .) and need to know what the volume would be at 0°C . (273°A .). One could, of course, go into the laboratory, cool the gas to 0° , and measure the volume at the lower temperature. More simply, one could reason from Charles' law that the *decrease* in volume is determined by the extent of the change in absolute temperature and use the two temperatures to set up a correction factor, thus,

$$\begin{aligned}
 \text{Volume at } 273^{\circ}\text{A.} &= \text{volume at } 298^{\circ}\text{A.} \times \frac{273}{298} \\
 &= 50 \times \frac{273}{298} \\
 &= 45.8 \text{ cc.}
 \end{aligned}$$

Why not multiply 50 by 298/273? Simply because this will lead to a volume greater than 50 cc., and we already know that the volume decreases with decrease in temperature.

The Influence of Pressure upon the Volume Occupied by a Gas.

It is immediately apparent that if one wishes to investigate the manner in which the volume occupied by a gas changes with change in pressure, the temperature must be held constant. According to the kinetic-molecular theory, the exertion of pressure upon a confined gas should force the gas molecules closer together, thus

reducing the unoccupied space between molecules. In other words, because of the availability of this free space, gases are compressible.

Once again, a simple experiment may be described to advantage. If, at some fixed temperature, a sample of gas is placed in a closed vessel equipped with a movable piston (so that the volume occupied by the gas can be changed), the change in volume occasioned by a change in pressure may be observed. When, as shown in Fig. 42, an initial pressure of one atmosphere is *increased* to two atmospheres, the volume occupied by the gas *decreases* by one-half. Similarly, if the pressure is increased to three atmospheres, the volume decreases to one-third of the original volume at one atmosphere. The relation between pressure and volume is seen to be an inverse one, *i.e.*, a change in either pressure or volume in one direction (increase or decrease) causes the other to change to the same extent but in the opposite direction.

Experimental findings such as those indicated above are typical of

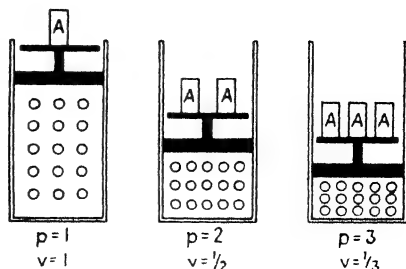


Figure 42. The relationship between the pressure exerted upon (or by) a confined gas and the volume that it occupies. The small circles represent gas molecules, and each of the weights labeled *A* represents a pressure of one atmosphere.

all gases. This regularity in the behavior of gaseous matter may be summarized by a descriptive statement first formulated by Robert Boyle (Fig. 43) in 1660 and known as Boyle's law: *The volume occupied by a definite weight of gas at constant temperature is inversely proportional*



Figure 43. Robert Boyle. (Courtesy of the Edgar F. Smith Memorial Collection, University of Pennsylvania.)

to the pressure. The utility and convenience of this generalization may be illustrated in a manner similar to that employed in the discussion of Charles' law. Suppose that we have a 50-cc. sample of a gas at 25°C. and a pressure of 760 mm. and it is required to know what the volume will be if the pressure is increased to 800 mm. without change in the temperature. Because we propose to *increase* the pressure, we know that the volume will *decrease*; from Boyle's law we know also that the extent of decrease in volume is proportional to the extent of the pressure change, and hence

$$\begin{aligned}\text{Volume at 800 mm.} &= \text{volume at 760 mm.} \times \frac{760}{800} \\ &= 50 \times \frac{760}{800} \\ &= 47.5 \text{ cc.}\end{aligned}$$

Simple arithmetic thus enables one to get information that otherwise could be had only by rather laborious and time-consuming laboratory procedures.

Manipulation of Gases in the Laboratory. The problem of handling gases in the laboratory is somewhat different from that involved in work with liquids and solids. Gases usually must be prevented from mixing with the surrounding atmosphere and consequently must be confined in suitable vessels. The most commonly employed procedure

for relatively simple experiments may be illustrated in terms of Fig. 44. A tube closed at one end is filled with a confining liquid (usually water or mercury) and inverted into a vessel containing the same liquid so that the tube is entirely filled. Gas, from any desired source, is admitted through the inlet tube, whence the gas bubbles up through and displaces the liquid in the tube. By such means, the sample of gas is collected in the upper part of the tube and is confined there owing to the presence of the liquid in the tube and in the lower container.

A more specific illustration will serve to focus attention upon still another problem. Assume that we must carry out an experiment in which a gas is produced in a chemical reaction and that our problem is to collect and measure the volume of gas formed. Assume further that we shall use a modified form of the apparatus shown in Fig. 44 by connecting the source of the gas to the inlet tube and shall use mercury as the confining liquid. After the gas sample has been collected in the tube, we need to know its volume, the temperature, and the pressure. The apparatus shown in Fig. 44 would have to be modified

so that we could adjust the level of the mercury in the outer vessel so that it will coincide with the level of the mercury inside the tube. When this is done, the pressure of the gas confined in the tube is the same as that of the atmosphere and the pressure may be obtained simply by reading the barometric pressure in the laboratory room. Similarly, if the gas sample is allowed to stand long enough so that its temperature will be the same as that of the surrounding atmosphere, the prevailing temperature in the laboratory is the same as that of the gas. Finally, by using a tube graduated in known units of volume, the volume of gas confined in the tube may be read directly.

In this fashion, it might be found, for example, that the chemical

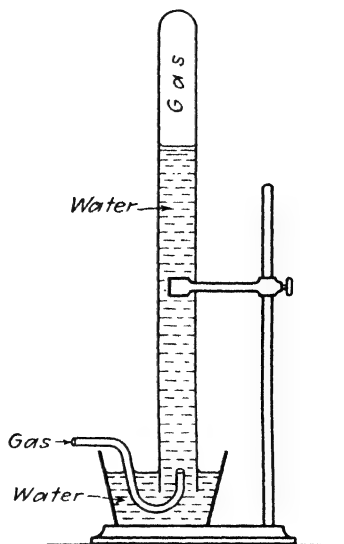


Figure 44. A type of apparatus that is used in the laboratory for the collection and confinement of samples of gases.

reaction in question produced 200 cc. of gas at 22°C. and a pressure of 746 mm. Now, suppose that another worker in a distant laboratory performed the same experiment. Would he also find that the reaction produced exactly 200 cc. of gas? Probably not, and for the reason that he would have measured the volume in a laboratory in which the temperature and barometric pressure were other than those given above. Volumes occupied by gases are meaningful only when the corresponding temperature and pressure are specified, and therefore the results of experiments involving gases must be compared only at the same temperature and the same pressure.

Standard Conditions of Temperature and Pressure. By international accord, scientists have agreed upon a temperature and pressure to be used uniformly as a basis for comparison of data relating to gas volumes. The temperature of 0°C. (that at which ice melts) and the pressure of 760 mm. (that of the atmosphere at sea level) are known as *standard conditions of temperature and pressure* (abbreviated S.T.P.). Accordingly, the problem becomes that of determining how the volume of 200 cc. will be changed if the pressure is changed from 746 to 760 mm. and the temperature is changed from 22°C. (295°A.) to 0°C. (273°A.). Stated otherwise, if the sample of gas occupies a volume of 200 cc. at 22°C. and 746 mm., what volume will the same quantity of gas occupy under standard conditions of temperature and pressure?

The answer to this question may be had readily by considering the problem in two steps, each of which employs the ideas embodied in the kinetic-molecular theory and a sequence of reasoning based upon the laws of Boyle and Charles. First, we propose to *increase* the pressure from 746 to 760 mm., and we know that the gas volume must *decrease*. In terms of Boyle's law, we also know that the extent of decrease in volume is related to the ratio 746/760. Similarly, the *decrease* in temperature from 295 to 273°A. must also result in a *decrease* in the volume of gas by an amount that is related to the ratio 273/295. Hence

$$\begin{aligned}\text{Volume at S.T.P.} &= 200 \times \frac{746}{760} \times \frac{273}{295} \\ &= 181.5 \text{ cc.}\end{aligned}$$

If both workers who performed the experiment followed correctly the

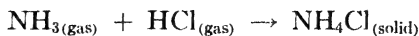
procedure outlined, both should get the same end result. The two values however might not turn out to be *exactly* the same. For example, one might find 181.2 cc. and the other 181.7 cc.; such differences are attributable to differences in the accuracy of the various measuring instruments employed, errors in observation made by the experimenters, and similar factors. Despite all the refinements in instrumentation, methods, and techniques that may be made, the numerical data therewith obtained as results of laboratory investigations seldom are in perfect agreement. Furthermore, no scientist worthy of the name ever places much faith in the results of a single experiment. One repeats the experiment again and again and thus gets several answers that are in as good agreement as the accuracy of the experimental methods permits. The average of these values is then taken as the best possible result.

In connection with laboratory work on gases, still another problem arises. Water is most commonly used as the confining liquid, except, of course, for those gases which dissolve in water to an appreciable extent. If, as shown in Fig. 44, a gas is collected over water, the gas sample will contain some water vapor. In terms of Dalton's law (Chapter 7) the total measured pressure will be that of the gas produced plus that due to the water vapor. The pressure exerted by water vapor at different temperatures has been measured very accurately and recorded in the scientific literature. A tabulation of some of these values is included in the Appendix. Consequently, one need only measure the total pressure of the mixed gases at a known temperature and then look up the vapor pressure of water (corresponding to the known temperature) and subtract this value from the measured barometric pressure. The result is the true partial pressure of the gas that was mixed with water vapor.

At about this point in the study of chemistry, the student whose major interests are non-technical begins to ask questions such as: "Why do I need to learn this stuff anyhow?" Although the teacher of science may be tempted to resort to the obvious answer that no one is really required to learn anything and is entirely privileged to remain in ignorance, a different viewpoint should be reflected. Students who do not intend to specialize in one or more phases of the exact sciences

are not expected to become expert in applying either the experimental methods or the principles of science. Nor are they expected for long to remember much of the subject matter encountered in so brief an exposure as is represented by the conventional introductory course. On the other hand, it is the hope of every sincere teacher of science that the student will at least develop a real appreciation of the *methods* of science and will acquire familiarity with a point of view and a method of attack which may well be applied with profit in non-technical areas of learning. These objectives may not be accomplished by reading about science, listening to learned lectures, or looking over the shoulder of someone actually engaged in scientific experimentation. In science, as elsewhere, *one learns by doing*. Only thus may anyone come to know of the scientist's careful attention to minute details, his devotion to the exact expression of ideas in terms of quantities, and his insistence upon the demonstrated reliability of experimental data. Only thus may one come to recognize the efforts expended by scientists in all of the various fields of endeavor in order that all of us may enjoy, for example, modern automobiles, travel by air, the cinema, and more comfortable homes and reap the benefits which accrue from work leading to new methods for the prevention and cure of disease.

The Diffusion of Gases. The fact that gas molecules move (diffuse) has already been emphasized, but not adequately. Again, it is helpful to study a property of matter in terms of a specific case, and the reaction that occurs when gaseous ammonia and gaseous hydrogen chloride are brought together provides a suitable basis for discussion. These two colorless gases unite to form a white solid known as ammonium chloride,



If, as shown in Fig. 45, a suitable source of ammonia gas is placed at one end of a long horizontal glass tube, a source of hydrogen chloride at the other, and the tube tightly stoppered, one would expect that each gas would diffuse toward the center of the tube, come into contact with each other, and thereupon combine to form the white solid which could be detected visually. Such is observed, but one finds that the white fog of ammonium chloride appears, not at the mid-point of the

tube, but somewhat nearer the end containing the source of hydrogen chloride. The inescapable conclusion is that the ammonia molecules diffused more rapidly than those of hydrogen chloride. As always, we make these observations and are then challenged to explain what we have seen to be experimentally demonstrated facts. In this instance, the kinetic-molecular theory provides the basis.

The theory holds that, at any particular temperature, the average kinetic energy of all kinds of gas molecules is the same. Therefore, the ammonia and hydrogen chloride molecules should move at the same rate if the kinetic energy were the only factor to be considered. It is quite apparent that the weights of the two kinds of molecules are different (mol. wt. of $\text{NH}_3 = 17$; mol. wt. of $\text{HCl} = 36.5$). Since the motivating power is the same in both cases, the lighter molecules

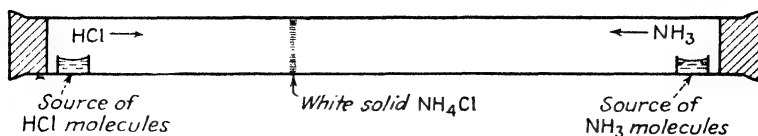


Figure 45. A simple demonstration of the diffusion of gases.

should certainly move the more rapidly. Disagreement with this line of reasoning would require one to defend the statement that the speed attainable by a passenger car would be the same as that attainable if the passenger-car motor were installed in a ten-ton truck.

The logical conclusion is that the rate of diffusion of gases is related to the masses of the gas molecules. In a more precise way, this conclusion is incorporated in Graham's law of diffusion, but this generalization need not be elaborated upon for present purposes. Suffice it to recognize that the study of rates of diffusion of gases in terms of Graham's law provides much useful information which may be expressed in terms of numerical data. For example, if, in the experiment just described, we measure the time from the start of the experiment to the first detection of ammonium chloride, then measure the distance from the source of each gas to the point of appearance of the white solid, we may calculate the *rate of diffusion* of each gas and express these rates in centimeters per second or in other suitable units. In addition, Graham's law provides a basis for the experimental determination of the molecular weights of gaseous substances.

EXERCISES

1. *New terms:* specific gravity, millimeter, centigrade, liter, diffusion, centimeter, relative density, cubic centimeter, absolute temperature scale, density, milliliter, standard conditions of temperature and pressure.
2. *Laws:* Charles' law, Boyle's law.
3. How does density usually change with change in physical state?
4. One sample of a gas is under a pressure of 1 atmosphere while another identical sample of the same gas is under a pressure of 1.5 atmospheres. In which case is the average distance between molecules the greater? Why?
5. What are the advantages and disadvantages in the use of mercury as the confining liquid for gases?
6. What is the reason for the establishment of a standard set of conditions of temperature and pressure?
7. What determines the rates at which gas molecules diffuse?
8. Assume that we have three identical samples of a gas, (1), (2), and (3), at the same temperature and pressure. If a decision can be made, state whether the volume will increase, decrease, or remain the same when (*a*) the temperature of sample (1) is increased and the pressure is decreased, (*b*) the temperature and pressure on sample (2) are both increased, and (*c*) the pressure on sample (3) is increased and the temperature decreased. Give reasons in each case.
9. What temperature on the Fahrenheit scale corresponds to 285° on the absolute scale?
10. A 10-cc. sample of a gas is at a temperature of 28°C . and a pressure of 700 mm. What volume will this gas occupy if the pressure is increased to 1400 mm. without change in temperature?
11. If the temperature of 126 cc. of gas at one atmosphere is increased from 0 to 100°C . without change in pressure, what volume will the gas occupy?
12. In a laboratory where the temperature was 25°C . and the barometric pressure was 755 mm., a sample of gas collected over mercury occupied a volume of 846 cc. What volume would this gas occupy under standard conditions?
13. Repeat exercise 12, but assume that the gas was collected over water instead of mercury.

COLLATERAL READING

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Properties of Matter in the Liquid and Solid States

IT HAS BEEN implied previously that one may acquire considerable information about gases merely by being observant and by thinking in terms of familiar occurrences. This is even more true of liquids and

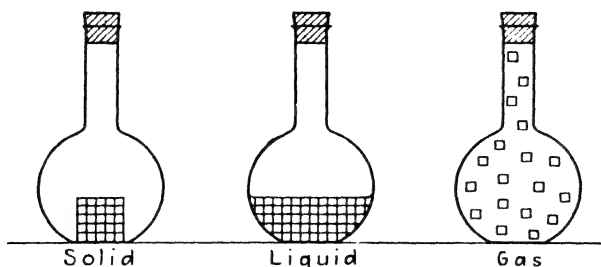


Figure 46. Solids retain their characteristic shape, liquids assume the shape of the containing vessel, while gases distribute themselves uniformly throughout the entire volume of the vessel.

solids. Whereas gases distribute themselves uniformly throughout the entire volume of vessels in which they are placed, liquids assume the shape of the vessel but solids retain their characteristic shape (Fig. 46). Everyone has observed that liquids are mobile in varying degrees, that they evaporate, boil, solidify, etc. Similarly we know that solids melt, that they exhibit different degrees of hardness, many are readily subject to fracture, some exist in crystalline forms of regular pattern, etc. In order to characterize matter in the liquid and solid states, however, it is necessary to deal with these and other properties more specifically. A proper understanding of the nature of matter in these physical states may be founded best upon the kinetic-molecular theory and an intercomparison with gases.

Properties of Liquids. One method whereby a gas may be changed to a liquid has been discussed in Chapter 8, *i.e.*, a lowering of the tem-

perature. The progressive decrease in temperature amounts to a withdrawal of energy, and the kinetic energy of the gas molecules decreases in a correspondingly regular fashion in accordance with Charles' law. As a result, the molecules move more and more slowly, and the average distance between molecules decreases. The gas comes to occupy smaller and still smaller volumes. If cooled to a sufficiently low temperature, the molecules come into close contact with other molecules and are held by the small force of attraction that molecules exert toward one another. At higher temperatures this force does not amount to much in relation to the kinetic energy, but when the latter is decreased to a very low value the force of attraction becomes the dominant factor. Large clusters of molecules are formed; and when they become large enough, small drops of liquid appear.

In the sense of the kinetic-molecular theory, it follows that liquids are much more dense than gases; the molecules in liquids are so close together that they can (and do) move through only extremely small distances before they collide with other molecules. Molecular motion in the liquid state is therefore drastically restricted in comparison with that possible in the gaseous state. It is evident also that the exertion of pressure upon a liquid can have but little influence upon the volume occupied by the liquid. Thus, liquids are essentially non-compressible; the molecules in liquids are already so close together that there is little available empty space into which the molecules may be further crowded by application of an external force.

Any gas may be changed to a liquid if the temperature is lowered enough to bring the molecules sufficiently close together. This, in turn, suggests another possible means of changing a gas to a liquid. Why not simply force the gas molecules closer and closer together by exerting upon them a great pressure? This is indeed a useful method, provided that the kinetic energy of the gas molecules is not prohibitively great (*i.e.*, if the temperature is not too high). For each gas there is a *characteristic* temperature above which the gas cannot be changed to a liquid (liquefied) solely by the application of pressure; this is called the *critical temperature*.

In industrial processes that require the liquefaction of gases, advantage usually is taken of both of these methods. The gas to be liquefied is subjected to high pressure, and at the same time the temperature is lowered.

Refrigeration. The energy changes that occur when gases are changed

to liquids, and vice versa, are utilized in refrigeration units such as commercial ice-manufacturing plants and electric refrigerators used in the home. Although the details of construction of the various kinds of commercial refrigeration equipment may be outwardly quite different,

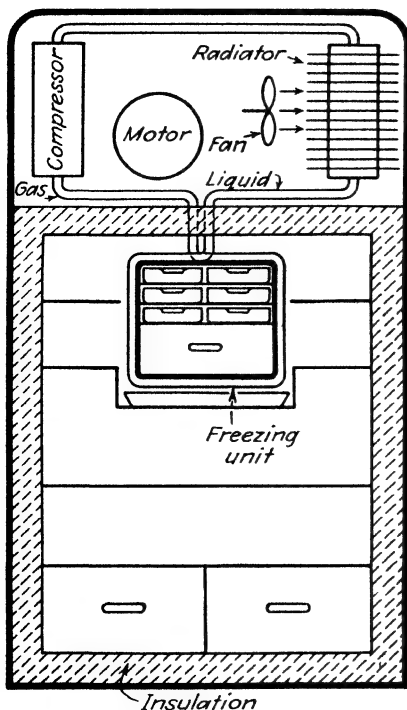


Figure 47. The essential features of an electric household refrigerator.

from the liquid to the gaseous state requires that heat be withdrawn from the surroundings. This part of the cycle takes place in the cooling coils that surround the relatively small freezing unit in the familiar household refrigerator. Because this compartment is relatively small and completely surrounded by the coils, it is cooled to a much lower temperature than the remainder of the interior space in the refrigerator.

The gas then moves outward from the expansion chamber and back to the compressor, where it then starts through another cycle. These cycles of operation are repeated over and over again until the desired low temperature is reached. The refrigerator is equipped with a device

different, the principles employed are essentially the same in all cases and may be illustrated by Fig. 47. The gas used in the refrigeration cycle must be one which can be liquefied easily and should be non-toxic so that it will not constitute a hazard in case of leakage. In a typical cycle of operation, the gas is compressed by means of a motor-driven compressor. Some of the energy expended in compressing the gas is imparted to the gas molecules, but this heat energy is dissipated by means of a radiator that is supplemented by a fan. The gas liquefies, and the liquid moves to the cooling unit where the liquid is allowed to evaporate and return to the gaseous state. Thereupon, the liquid is cooled (by evaporation), and the continuing transfer of matter

known as a *thermostat*; this is simply an automatic temperature regulator which stops the compressor motor and fan when the predetermined low temperature is reached and starts them running again when the temperature rises above this value. The principle of operation of the thermostat has its basis in the fact that certain solids expand and contract considerably with changes in temperature. As shown in Fig. 48, a contact strip *A* is moved on a pivot at *B* through the action of a coiled rod *C* which coils and uncoils with change in temperature. Strip *A* makes electrical contact at *D* and starts the motor whenever the temperature rises to that set by the regulating knob *E*, which also controls the position of the electrical contact *D*.

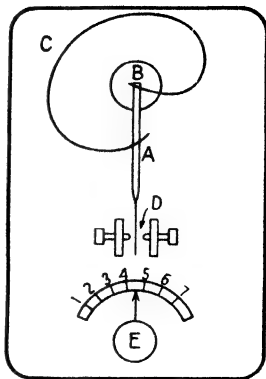
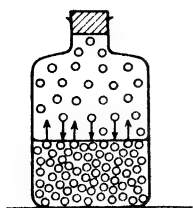


Figure 48. A simple type of thermostat.

Gases commonly used in refrigeration cycles include ammonia (NH_3), sulfur dioxide (SO_2), and a group of related organic gases usually referred to simply by the general term Freon (see Chapter 26).

Vapor Pressure. Regardless of their chemical composition, all liquids show some tendency to evaporate (change from the liquid to the gaseous state). The vapor pressure of a liquid is a measure of its tendency to evaporate. Any observant person knows that hot water evaporates more rapidly than cold water, that water evaporates more rapidly into a dry atmosphere than into a humid one, that water does not evaporate completely from a closed container, that cigarette-lighter fluid evaporates more readily than water, etc. Like water, all liquids evaporate but at different rates, which are dependent upon temperature.



o = Water molecules

Figure 49. Liquid water and water vapor exist in a condition of dynamic equilibrium in a closed container.

If, for example, water is placed in a closed container as shown in Fig. 49, some water molecules escape from the liquid and exist admixed with the air above the liquid. Those molecules which escape must be ones in the surface of the liquid which happen to have kinetic energies a little greater than the average. At any given temperature the quantity of water that will exist in the

gas above the liquid is limited; and as more and more water molecules pass into the gaseous condition, more and more molecules in their motion through space strike the surface of and re-enter the liquid state. Finally there is realized a condition such that the number of molecules re-entering the liquid per unit of time is the same as the number leaving. This is just another example of a reversible process in which two physical changes (liquid \rightarrow gas, and gas \rightarrow liquid) occur simultaneously and at the same rate. The two counterbalance each other, and there is no net change even though the changes do continue to occur. This is the condition known as *dynamic equilibrium*; other examples will be encountered.

Boiling Point. Since the atmosphere exerts pressure upon the surface of a liquid, the escaping tendency of molecules in the surface of the liquid is opposed by the atmospheric pressure. If, however, the temperature of a liquid is raised, its vapor pressure may be increased enough so that the vapor pressure of the liquid will be greater than the opposing atmospheric pressure. The temperature at which this occurs is the so-called *boiling point* (b.p.) of the liquid.

The boiling points of pure liquids vary greatly depending upon the chemical nature of the compounds in question. Some liquids boil at very low temperatures; some boil at very high temperatures. The boiling point of a pure liquid is a characteristic property, is usually easy to determine experimentally, and hence is a property useful for purposes of identification.

It is obvious that the boiling points of liquids depend upon the prevailing atmospheric pressure. At standard pressure, water boils at 100°C. , but it boils at much lower temperatures (*e.g.*, as low as 70°C.) at altitudes high in the mountains, where the opposing atmospheric pressure is much less. The stories about the length of time required to prepare boiled eggs at high elevations are true enough, even though the popular explanations offered usually leave something to be desired. The simple truth is that it takes longer to cook the eggs because the water is not so hot when it boils.

Freezing Point. Just as there are characteristic temperatures at which pure liquids boil, so there are equally characteristic temperatures at which they solidify, or freeze. The *freezing point* (f.p.) of any pure liquid is another of those physical properties which are very useful in establishing the identity of pure substances. Consider, for example,

that we are given a pure liquid and asked to identify it. In addition to chemical analysis, we should resort to the measurement of—for instance—its density, boiling point, and freezing point. We could then refer to the chemical literature and find out what pure liquid compound meets all of the specifications found by these experiments. It would be highly improbable that any doubt could remain; no two liquids would be expected to have identical values for so many different physical properties.

In terms of the kinetic-molecular theory, the progressive cooling of a liquid amounts to a withdrawal of heat and therefore a lowering of the kinetic energy of the molecules of the liquid. The molecules in the liquid are already drastically restricted so far as their movement is concerned, and they become still further restricted as the temperature is progressively lowered. When the temperature reaches the freezing point of the liquid, the attractive force between the molecules orients them into the definite pattern of arrangement in space that characterizes the crystal that separates. Although it is possible to formulate a somewhat better definition, we may consider the freezing point of a liquid to be the temperature at which it changes to the solid state.

Physical properties of pure substances constitute information useful for purposes other than identification. Essentially all applications to practical uses must take into account the particular physical properties of the liquid under consideration. A liquid that otherwise might appear to be potentially very desirable for use as an “antifreeze” in automobile radiators might be ruled out because it has too low a boiling point. Similarly, a possibly useful lubricant liquid might have to be rejected because its freezing point is too high to permit its use in cold climates.

Viscosity. Another characteristic property of liquids is their viscosity, which may be defined as resistance to flow. Some liquids such as tar and molasses are so viscous that they may be poured from one container to another only very slowly and incompletely; others are quite fluid and flow more readily. Honey kept for a time in the refrigerator becomes very viscous, but its viscosity decreases as it is warmed to room temperature. The lubricating oil in automobile motors increases in viscosity during a cold night and offers great resistance to the moving parts when one attempts to start the cold motor.

From such simple observations one may decide that, in general, the viscosity of a liquid decreases with increase in the temperature. This

alone, however, does not account for the fact that different liquids show such marked differences in viscosity. The viscosity of liquids may be thought of as a manifestation of internal friction in the body of the liquid. The extent to which any liquid will exhibit viscosity is therefore dependent upon such factors as the size and shape of the molecules, the distance between molecules, etc., and only incidentally dependent upon the nature of the atoms that make up the molecule. From crude petroleum there are obtained several different commercial

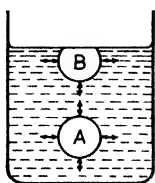


Figure 50. A comparison of a molecule in the body of a liquid and one in the surface layer.

products that contain only the elements carbon and hydrogen. These include gasoline, lubricating oil, and vaseline. That these three products show a wide range of viscosity is a matter of common knowledge.

There are, of course, numerous well-established methods whereby the viscosity of liquids may be measured in the laboratory, and there are bases for expressing the resulting data in terms of suitable numerical values. Correlation of viscosity data with the nature of the respective chemical formulas permits one to make useful predictions relative to the viscosity of new liquids, the manner in which this property will change with change in temperature, etc.

Surface Tension. The property of liquids that is known as surface tension is one that most persons find difficult to visualize. A familiar observation may provide a useful basis for discussion. We have all observed that drops of water (and most other liquids as well) tend to assume a nearly spherical shape. This is the shape that entails the smallest possible exposed surface for any given volume. It is as though there were present a force acting from the center of the drop and pulling all the molecules toward the center. One might also think of surface-tension effects as being of the sort that would result if the surfaces of liquids were covered by an elastic skin.

More progress may be made toward an understanding of surface tension by thinking in terms of the attractive forces between molecules in the liquid state. Once again, the kinetic-molecular theory may be utilized. In the body of a liquid, a molecule *A* is completely surrounded by other like molecules and thus is subjected to attractive forces that are of equal magnitude in all directions (Fig. 50). A molecule *B* in the surface layer, however, experiences no such balance of forces. Mole-

cule B is attracted by forces that are unequally distributed since there are no molecules of the liquid directly above B . Hence, the net result is a tendency for B to be pulled toward the interior of the liquid.

While surface tension may be measured accurately and expressed in numerical units, it is a property that is relatively little used as a means of characterizing pure liquids. This property is nevertheless important. It is in part because of surface tension that oil rises in a lampwick, that a steel needle floats on water if placed there so that the surface is not penetrated, that liquids rise in capillary tubes, etc. The cleansing action of soap is largely related to the manner in which the soap influences the surface tension of water.

Properties of Solids. Mention has been made of the nature of the changes that occur when a liquid is cooled to its freezing temperature. The transition from liquid to solid causes the atoms or molecules to assume more or less fixed positions in space relative to one another. The net result is a still greater restriction on molecular motion. The structural units in solids may be atoms, molecules, or ions, and their motion may be thought of as a vibration about a fixed position. This, however, is somewhat inaccurate, for it can be demonstrated that the structural units in solids are capable of diffusion, albeit at exceedingly slow rates. Whereas the diffusion of a gas molecule through a given distance might occur in a fraction of a second, that of a molecule in the solid state would require many years to traverse the same distance.

It has already been pointed out that density is a characteristic property of solids and at least implied that solids are relatively non-compressible. Before entering upon further discussion of these and other specific properties of solids, it is necessary to recognize that there are two broad classes of solid substances, *i.e.*, *crystalline* solids and *amorphous* solids. The discussion which follows immediately is restricted to crystalline solids; those which are amorphous in character will be treated separately.

Melting Point. In an effort to visualize what happens when a solid such as ice melts, it is helpful to return to the ideas that the molecules in the solid occupy essentially fixed positions in space, that solids are dense, closely packed materials, but that the molecules are capable of very restricted motion. If, by the application of heat, the kinetic energy of the molecules is increased, they should "vibrate" through greater and greater distances. At some temperature, the kinetic energy

should become great enough so that the individual molecules should be able to break away from the surrounding attractive forces and enjoy the relatively greater freedom of motion which characterizes the liquid state. The temperature at which this occurs is called the *melting point* of the solid.

The melting point of any pure substance corresponds to the change: solid \rightarrow liquid. The freezing point of the same substance similarly relates to: liquid \rightarrow solid. The two processes therefore occur at the same temperature.

In the case of crystalline solids, the melting point is a very definite reproducible property that is readily measurable. Particularly in the field of organic chemistry, there is no single property of solids that is more widely used to establish the identity and purity of compounds. Most inorganic compounds, on the other hand, melt at temperatures that are inconveniently high for easy measurement in the laboratory.

Hardness. The quality of hardness is that of being firm and unyielding toward forces which tend to produce distortion. Anyone who has ever compared the metals iron and lead knows that the latter is a relatively soft metal.

In chemistry, hardness is a property that is given but little attention. It is, however, a very important and much used property in the fields of metallurgy and mineralogy. Hardness is expressed usually in terms of some wholly arbitrary "scale of hardness." Such scales are based upon relative hardness and are related to specific substances that cover a wide range of hardness. A scale commonly used in mineralogy is that given in Table 4. Thus the mineral orthoclase is harder than (and

TABLE 4. Mohs' Scale of Hardness

<i>Substance</i>	<i>Hardness</i>	<i>Substance</i>	<i>Hardness</i>
Talc.....	1	Orthoclase.....	6
Gypsum.....	2	Quartz.....	7
Calcite.....	3	Topaz.....	8
Fluorite.....	4	Corundum.....	9
Apatite.....	5	Diamond.....	10

will scratch the surface of) the mineral apatite but is less hard than quartz. The position of diamond as the hardest substance included in the scale is of particular interest, and this matter will come up again in another connection.

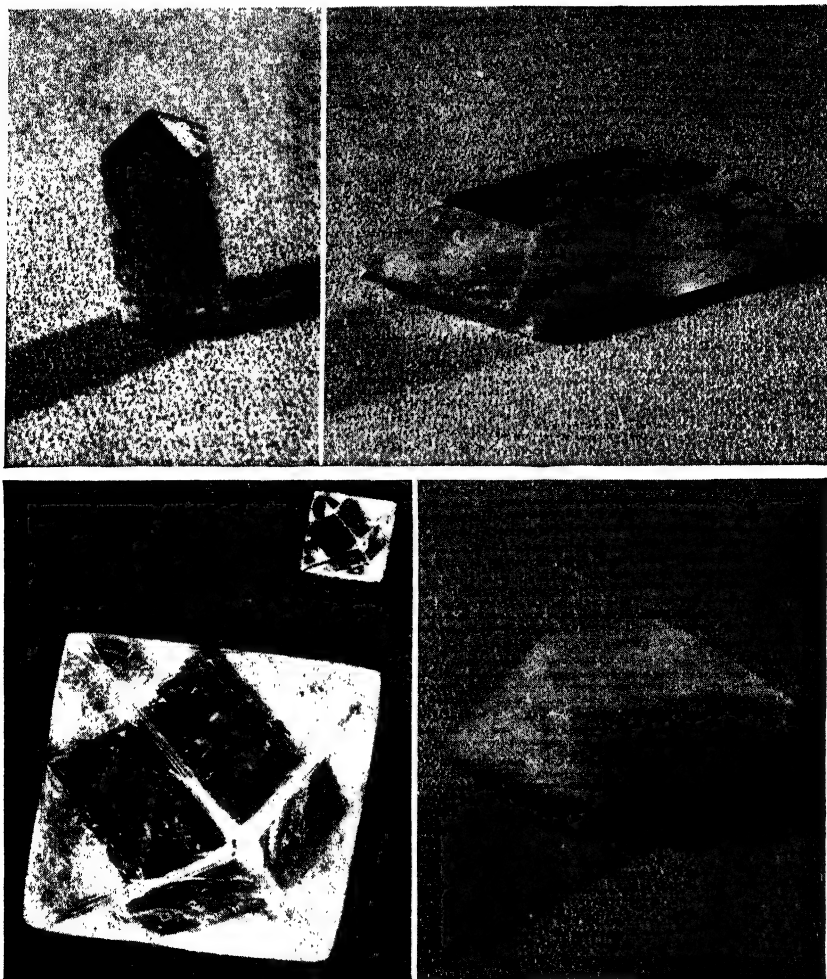


Figure 51. Some typical crystal forms. (Courtesy of Ward's Natural Science Establishment, Inc.)

Crystalline Structures. Solid matter classed as crystalline is characterized by definite external shape that represents symmetrical arrangement of the structural units. Some crystals are cubic or rectangular, others are like long cylindrical needles, still others take the form of flat plates or leaf-like structures. In any case it appears that the atoms, molecules, or ions which make up the crystal assume fixed positions

which conform to some predetermined pattern and give rise to a precise geometry of arrangement. The crystal forms shown in Fig. 51 are typical.

Largely through the use of purely physical rather than chemical methods, much has been learned about the internal architecture of crystalline solids. This is the science of *crystallography*, which has contributed much information that has proved to be extremely useful in the understanding of difficult problems in related fields such as chemistry, physics, and metallurgy. Based upon the geometry that typifies the symmetry of arrangement of the structural units, all crystalline solids are organized into 32 crystal classes.

One should not be misled into believing that solid substances commonly encountered are necessarily in their characteristic crystalline form. This may have been altered either deliberately or accidentally. Diamond crystals, for example, are cut, ground, and polished so that light will be refracted and reflected in a manner that enhances the color and sparkle. Quartz crystals in the form of ordinary sand are often nearly spherical in shape, but only because of abrasion due to many contacts with hard objects.

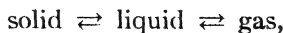
Other Properties of Solids. There seems no need to pursue further the study of specific properties of solids. Many others might be considered, *e.g.*, compressibility, thermal and electrical conductivity, abrasive properties, etc.

Amorphous Solids. This designation is sort of a catchall classification that includes all solids that are not crystalline. In a purely literal sense, the term amorphous means *without form*.

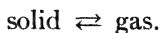
There is ample justification for the view that amorphous substances represent a condition intermediate between the solid state and the liquid state. Amorphous bodies are liquids that are inelastic, rigid, or of very high viscosity. Lampblack, pitch, *glass*, and rosin are typical examples. When an amorphous solid is heated, it does not melt at a definite temperature. Rather, it softens gradually over a considerable temperature interval and finally assumes the properties that are typical of the liquid state. In amorphous bodies there is no orderly geometric arrangement of structural units.

Sublimation. The vapor pressure of most solids at ordinary temperatures is so low that it may be ignored for most practical purposes. There are some notable exceptions. These solids have surprisingly high

vapor pressures and evaporate directly into the gaseous state without first melting to form liquids. Also, the gases condense directly to the solid state, and again the liquid state is by-passed. These changes are referred to as *sublimation*, and the solid is said to sublime. Whereas the usual sequence of reversible changes is



solids that sublime follow the course



Familiar examples of solids that sublime include camphor, iodine, and two solids that are ordinarily used as moth balls or moth crystals. These are the organic compounds *naphthalene* (C_{10}H_8) and *paradichlorobenzene* ($\text{C}_6\text{H}_4\text{Cl}_2$). With both of these compounds the rate of sublimation is favorable to the maintenance of a high concentration of the repellent in the gaseous state over a considerable period of time.

EXERCISES

1. *New terms*: melting point, critical temperature, thermostat, boiling point, crystalline solid, sublimation, dynamic equilibrium, surface tension, viscosity, vapor pressure, amorphous solid, freezing point.
2. On the basis of the kinetic-molecular theory, explain what happens when (a) solids melt; (b) liquids evaporate.
3. Distinguish between amorphous and crystalline solids.
4. Cite two methods whereby a gas may be liquefied.
5. Trace the changes that occur during a cycle of operation of a household refrigeration unit.
6. Why, during ascent of a mountain road, does water in an automobile radiator boil, whereas it did not boil prior to the ascent even though the motor was operating at the same temperature?
7. Upon what principle does the operation of a thermostat rest?
8. Compare gases, liquids, and solids from the standpoint of (a) the extent to which molecular motion is possible; (b) density; (c) compressibility.

9. How does each of the following properties of pure liquids change with change in temperature: (a) viscosity, (b) boiling point, (c) vapor pressure?
10. If a liquid is to be used in a radiator antifreeze mixture with water, should its vapor pressure be greater or less than that of water? Why?

COLLATERAL READING

BABOR and LEHRMAN: "Introductory College Chemistry," The Thomas Y. Crowell Company, New York, 1941, Chapter 22.

RAY: "General Chemistry," J. B. Lippincott Company, Philadelphia, 1947, Chapter 31.

SCHOCH, FELSING, and WATT: "General Chemistry," McGraw-Hill Book Company, Inc., New York, 1946, Chapter VI.

TIMM: "General Chemistry," McGraw-Hill Book Company, Inc., New York, 1944, Chapters 14, 15, and 16.

Hydrogen

IT IS ESSENTIAL that a few of the elements be studied in sufficient detail to illustrate the kinds of information available for nearly all of the known elements. In the light of their relative importance, hydrogen and oxygen are rather obvious choices. The amount of time typically available necessitates the omission of all but a few of the major features of the chemistry of these and other elements. It is well to recall, how-

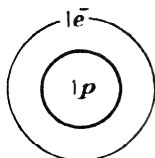


Figure 52. Diagram representing the structure of the hydrogen atom.

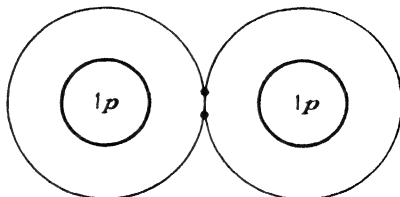


Figure 53. Diagram representing the structure of the hydrogen molecule. (Each black dot represents one electron.)

ever, that the periodic arrangement of the elements serves as a basis for the extension to other elements of the knowledge gained about a more limited number. In the discussions which follow, special emphasis will be placed upon those phases of the chemistry of hydrogen which are of major day-to-day importance.

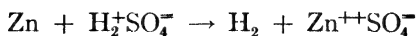
The hydrogen atom consists of a single proton in the nucleus and one extranuclear electron (Fig. 52); this element normally exists in the form of the covalent diatomic molecule represented by Fig. 53. In most of its compounds, hydrogen is joined to other elements by the process of sharing of electrons, but in some cases the chemical union is largely ionic in character.

Methods for the Preparation of Hydrogen. When the chemist speaks of "preparing" an element or a compound, he means the pro-

duction (from any suitable source) of a sample of the substance in a quantity and degree of purity which are dependent upon the use to which the sample is to be put. If one wishes a small sample of high purity, typical laboratory-scale methods are employed and questions of convenience take precedence over considerations of cost. Where large-scale operations that entail critical economic factors are involved, cost is more often the determinant in the choice of method. Accordingly, we shall recognize a distinction between what may be called *laboratory methods* and *commercial methods* for the preparation of chemical substances. Further, it should be noted that any given method may or may not be adaptable to both situations.

With reference to laboratory methods for the preparation of hydrogen, the liberation of hydrogen by the action of an electric current upon water has been cited earlier. This procedure, of course, also produces oxygen, and arrangement may be made to collect the two gases separately. This, like all other methods for producing hydrogen either commercially or in the laboratory, entails the decomposition of a compound of hydrogen.

By all odds the simplest and most convenient method for the laboratory-scale preparation employs the kind of chemical reaction that occurs when a suitable metal is treated with an appropriate acid. From a wide selection of possibilities, the addition of sulfuric acid (the acid used in automobile storage batteries) to the metal zinc in the presence of water is the one most often used. The equation for this reaction is



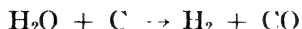
In this reaction, the neutral zinc atom, which has two electrons in its outermost shell, loses these electrons and becomes a zinc ion. Each of the two hydrogen ions of the acid gains one of the two electrons lost by the zinc. Thus, each hydrogen ion becomes a neutral hydrogen atom, and the two then share electrons to form the gaseous hydrogen molecule. The positive zinc ions are electrically counterbalanced by the negative SO_4^{--} ions. It may be concluded that in this reaction the zinc *displaces* the hydrogen from its combination in the form known as sulfuric acid.

In the language of chemistry, reactions that take place by virtue of loss and gain of electrons are classified as oxidation-reduction reac-

tions. *Oxidation is defined as the loss of electrons; reduction is the term applied to the gain of electrons.*

By no means all acids or all metals are suitable for the preparation of hydrogen. Some metal-acid combinations do not react at all, some react but form products that do not include hydrogen, while still others react at rates that are impractical. In view of the fact that there are so many different acids and different metals, it follows that the problem of choosing a suitable metal and acid for the preparation of hydrogen can become somewhat complicated. While there is no wish to belabor the point unduly, the student should appreciate that the chemical literature includes a wealth of information which obviates much of the apparent complexity of the problem.

In commercial practice, the electrolytic decomposition of water is a suitable method but one that is at economic disadvantage. There are several commercial methods that are superior. One involves a very simple reaction between water and the element carbon,



but this reaction produces two gaseous products (hydrogen and carbon monoxide—this mixture is known commercially as *water gas*), and so we are now faced with the problem of separating the two. We might suggest that the mixture be bubbled through water and hope that the carbon monoxide would dissolve in the water and that the hydrogen would not do so. This would be a feasible suggestion were it not for the knowledge that both hydrogen and carbon monoxide dissolve in water, but only to a very limited extent. If we want to separate two chemical substances, we must take advantage of some *difference* in their chemical or physical properties. Hydrogen and carbon monoxide are just too similar to make for easy separation.

The solution to this particular problem is found, not by devising a direct means of separation of these two gases, but rather by changing the carbon monoxide to another gas that can be separated from hydrogen more simply. The carbon monoxide is changed to carbon dioxide by the reaction



in which the H_2O is in the form of steam. First of all it should be noticed that we now have twice as much hydrogen as before, *i.e.*, that

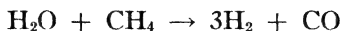
formed in the first reaction plus an equal quantity formed in the second. Next, we need only know that the mixture of CO_2 and H_2 may be separated by subjecting the mixture to pressure in the presence of water. Thereupon, the CO_2 dissolves in the water, and very nearly pure hydrogen remains as a gas.

Catalysts and Inhibitors. Attention must be given to still another problem. If one should attempt to carry out the reaction represented by the preceding equation without having some additional information, the experiment would be an utter failure. The mixture of hydrogen, carbon monoxide, and steam simply would not react at any detectable rate. If, on the other hand, we should add to the reaction mixture a little of the compound called nickel oxide (NiO), the reaction would occur readily and at a practical rate. The really striking fact is that, when the reaction is completed, the nickel oxide remains and is apparently unchanged. This is not at all an uncommon occurrence and is one of the aspects that to the uninitiated seems to endow chemistry with the flavor of witchcraft. One may rightfully be skeptical that a foreign substance, merely by its presence, changes so drastically the rate of an otherwise immeasurably slow chemical change.

This case is a typical illustration of the phenomenon of *catalysis*, and the nickel oxide is called a *catalyst*. Although it is difficult to formulate a satisfactory and unambiguous definition, a catalyst may be said to be a substance that increases the rate of a chemical reaction without itself being consumed in the course of the reaction. In a similar but opposite role there are substances that *decrease* the rates of chemical reactions; these are called *inhibitors* or *retarders*. Common applications of inhibitors include the use of specific chemicals to decrease the rates of corrosion ("rusting") of metals, deterioration of rubber products owing to reaction with the oxygen of the atmosphere, deterioration of food and drug products (*i.e.*, "food preservatives"), etc. It is usually true that the action of catalysts and inhibitors is remarkably specific. Just because a given element or compound acts as a catalyst for one reaction does not imply that it would be at all useful in connection with some different reaction. Under these circumstances one may rightfully wonder how catalysts and inhibitors are discovered for these very specific applications. There are many stories about chemists having discovered catalysts or inhibitors either through sheer accident or as a result of otherwise unfortunate errors. These cases are

the exceptions. While many aspects of the function of catalysts and inhibitors are still obscure and much remains to be learned about them, enough is known to permit one to search for catalysts and inhibitors on the basis of an intelligent and carefully planned program of investigation.

After this rather lengthy digression, attention must again be directed to another method for the production of hydrogen. Although several might be included, only two need be mentioned specifically. This is the process whereby methane (the chief component of natural gas) and steam react at very high temperatures in the presence of a catalyst.



As described above, separation of the hydrogen is accomplished following conversion of CO to CO₂.

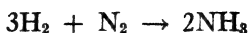
Hydrogen is also produced on a large scale by both thermal and catalytic decomposition of methane.



All of these commercial methods possess features that are common to essentially all processes used for the large-scale production of chemicals. They (1) involve simple chemical changes, (2) employ cheap and abundant raw materials, and (3) produce usable by-products in addition to the product of primary interest.

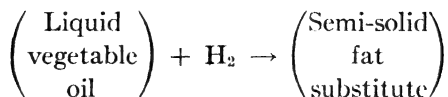
Properties of Hydrogen. The element hydrogen is the lightest known chemical substance. This colorless, odorless, tasteless, and highly flammable gas may exist also as a solid that melts at the very low temperature of $-259.2^\circ\text{C}.$, and the resulting liquid boils at $-252.8^\circ\text{C}.$ At $20^\circ\text{C}.$, hydrogen dissolves in water to the extent of a little less than 2 cc. of the gas per 100 ml. of water.

The chemical properties of hydrogen have been studied extensively. Hydrogen combines with many of the other elements to form a class of compounds called *hydrides*. Many of the compounds in this category have common names such as water and ammonia; the formation of both is shown by the following equations.



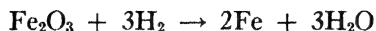
The reactions represented by these two equations involve nothing more than the direct union of different kinds of elements, and these two compounds are formed largely by virtue of the process of sharing of electrons.

Hydrogen may combine directly also with compounds. The reactions of this type that are of major practical importance involve hydrogen and certain types of organic compounds. Since these reactions may not be understood properly until one gains at least a limited knowledge of the nature of the organic substances concerned, it is adequate for the present to indicate these changes only schematically.



Such reactions are referred to as *hydrogenation* and employ finely divided metallic nickel as a catalyst. Familiar products thus produced are oleomargarine, Crisco, Spry, and the like. In a similar fashion, coal may be hydrogenated to provide a mixture of liquid products from which are obtained gasoline substitutes and a variety of other useful materials. It is entirely within the realm of possibility that, should our petroleum resources become depleted, the hydrogenation of coal could provide an ample supply of motor fuels.

Another important chemical property of hydrogen is concerned with the manner in which it reacts with compounds and removes one or more elements from the compound. For example, the oxygen in iron oxide may be removed as shown by the equation



and the metallic iron thereby liberated from its compound with oxygen. It is clear why such reactions of hydrogen are of considerable importance. Not only do reactions of this kind provide a convenient laboratory method for the preparation of certain elements (usually metals) from their compounds, but also these reactions are adaptable to large-scale commercial use.

Uses of Hydrogen. The preceding discussion of chemical properties includes some of the important uses for this element, *e.g.*, in the hydro-

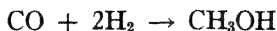
generation of animal or vegetable oils and of coal; in the production of metals from their compounds; and in the manufacture of compounds such as ammonia. The latter is used in numerous ways that will be discussed later in this book; ammonia is manufactured in very large quantities, and this, of course, requires much hydrogen. This element is also used directly or indirectly in the commercial manufacture of so



Figure 54. The burning of the German Zeppelin Hindenburg. (*Courtesy of Acme Newspictures.*)

many different and useful substances that only typical examples can be included here.

From carbon monoxide and hydrogen in the presence of a catalyst, methyl alcohol ("wood alcohol") is produced.



This is a typical example of the manner in which chemical research supplies the things which are necessary to industrial progress. As sug-

gested by its common name, this alcohol has long been produced from wood, but the cost was high and the supply never equal to the potential demand. About twenty years ago, another method for the manufacture of methyl alcohol was perfected, and it was based upon a thorough scientific investigation of the reaction represented by the preceding equation. It was found that certain compounds of copper, zinc, chromium, etc., act as catalysts and that temperatures in the range 350 to 600°C. and pressures of 100 to 200 atmospheres are favorable to the occurrence of this reaction. With an optimum balance of conditions of temperature, pressure, and catalysis, this reaction permits the efficient manufacture of high-purity methyl alcohol at less than half the cost of production from wood. Thus, the methods of science produce in the laboratory a procedure for the formation of a substance that otherwise must be obtained from natural sources. Furthermore, the low cost of the product of laboratory origin is reflected in a lower market price, and this in turn leads to much wider use in industry.

There are numerous other important uses for hydrogen. It is used as a fuel in the "atomic hydrogen torch," which gives temperatures high enough to melt even metals such as tungsten (m.p., 3,370°C.). To a limited extent, hydrogen is still used to inflate balloons, and the like, but the explosion hazard (Fig. 54) is so great that this practice is inadvisable.

Factors That Determine the Rates at Which Chemical Reactions Occur. At least by inference, there have already been mentioned a few cases which suggest that the question of the rates at which chemical reactions occur is a matter of major concern to the chemist. If one seeks the product of a given reaction in either the laboratory or the industrial manufacturing plant, it is self-evident that the reaction should be one that proceeds at a practically rapid rate. Conversely, the utility of a reaction may be dependent upon our ability to prevent the reaction from taking place too rapidly. We have seen how catalysts and inhibitors may be utilized to achieve these ends, and their role does not require further elaboration. Three other factors, however, need to be considered in detail because they are the working tools whereby the chemist exercises control over chemical changes.

The Specific Properties of the Reactants. As a suitable basis for discussion, we may return to the earlier statement that all metals do not

react with acids at the same rate. If, for example, we should add hydrochloric acid to samples of the metals zinc, copper, and lead, we should find that zinc reacts the most rapidly, lead next, and copper least rapidly. We should find exactly the same order of relative rate of reaction if we should examine the rates at which these three metals react with chemicals other than acids. It would therefore appear that the speed with which any substance reacts is an inherent property of the material in question. Such is indeed the case.

The interaction of metals and acids are oxidation-reduction reactions in which the neutral metal atoms lose electrons. The rate at which any given metal reacts is accordingly related to the structure of its atoms. Of the three mentioned, zinc reacts the most rapidly because the two electrons in the outermost shell are held the least firmly; in other words, the zinc atom loses electrons relatively readily and hence shows a great tendency to participate in chemical change. Similarly, lead atoms lose electrons less readily than zinc atoms but more readily than copper atoms, which are very reluctant to part with their electrons. This sort of interpretation is consistent with observations that all have made at one time or another. The relatively active metal iron rusts (corrodes, tarnishes) much more rapidly than the more inactive metals such as silver, gold, and platinum. It is because of their low rates of reaction with atmospheric gases and other substances with which they may come into contact that the latter metals are used in the fabrication of jewelry, etc.

It may be concluded that each element and compound is characterized by a specific reaction tendency. Since this is a property inherent in the nature of the chemical substance, we cannot do much about this particular factor in relation to controlling rate of reaction. We may, on the other hand, select at the outset a substance that is known to have a favorable combination of properties for the purpose at hand. There are, for example, means whereby one may measure the quantities of energy required to remove electrons from different kinds of atoms. Through the use of this kind of information, one may at least start out on the basis of an intelligent selection of reacting materials.

Temperature. Exercise of control over the temperature at which chemical changes occur is probably the most useful approach used by the chemist and engineer. If two substances react at a certain rate at room temperature, we should reason from the kinetic-molecular theory

that they should react at a greater velocity at a higher temperature. When the temperature is elevated by supplying energy in the form of heat, the kinetic energy of the molecules is increased. Consequently the molecules move more rapidly, they collide with each other more frequently, and they thus have an enhanced opportunity for reaction. By way of a very rough estimate, one may assume that, if a reaction occurs at a certain velocity at or near room temperature, the rate will be approximately doubled when the temperature is raised 10°C . This is not too surprising when it is considered that going from 25 to 35° represents a fairly large percentage increase in temperature. This general rule would not be expected to hold true if, for instance, the temperature were increased from 1000 to 1010°C .

The control of reaction rate through the control of temperature must take into account the fact that all chemical changes are accompanied by characteristic energy changes. These energy changes commonly (but not always) involve the liberation or the absorption of heat energy. Chemical reactions that liberate heat are called *exothermal* reactions; those which absorb heat are said to be *endothermal*.

Concentration. The term concentration denotes the degree to which matter is crowded into a given volume in space. Concentration may be expressed in terms of the total weight of matter contained in any specified volume or in terms of the number of individual units contained in that volume. We might choose, for example, to express the concentration of students in classrooms in terms of their total weight per classroom or as the number of individual students per classroom. How we should do it depends upon the purpose at hand. Total weight would be best if we were concerned with the structural safety of the building; the other basis would serve better if we were interested in the ratio of students to teachers.

So it is with atoms and molecules. For some scientific purposes, one needs to know the total weight of matter per unit of volume (*simple concentration*); in other cases it is necessary to know the number of molecules per unit volume (*molecular concentration*).

From earlier discussions of gases, it follows that the concentration of gases may be increased by increasing the pressure. Thereby, the gas molecules are caused to occupy smaller volumes, and thus there are more molecules per unit of volume. At the greater concentration the molecules are closer together and do not have to move through such

great distances before they collide (and react) with other molecules. The situation is somewhat different in the case of solids; a solid reacts primarily at its exposed surfaces. We have all observed that a large lump of coal burns slowly, whereas coal dust burns at a very great rate and this is the major factor involved in many of the explosions that have occurred in coal mines. Accordingly, the *state of subdivision* is an important variable where solids are concerned, and one may follow the general rule that, the more finely divided the solid, the greater will be its rate of reaction.

The discussion of concentration as applied to substances dissolved in liquids (or in other media) will be deferred to Chapter 13.

The Law of Mass Action. The influence of concentration upon the velocity of chemical changes is summarized in the general statement that is variously referred to as the law of mass action, the law of molecular concentration, or simply the mass law: *The rate at which a chemical reaction takes place is directly dependent upon the molecular concentrations of the reacting substances.* This law was first stated in somewhat different terms in 1867 by the Norwegian chemists Guldberg and Waage. It is susceptible to expression in rigorous mathematical form and is at the same time one of the most important and useful concepts that the chemist has at his command.

EXERCISES

1. *New terms:* molecular concentration, hydrogenation, oxidation, catalyst, endothermal reaction, reduction, hydride, exothermal reaction, simple concentration, water gas, inhibitor.
2. *Law:* The law of mass action.
3. On the basis of the kinetic-molecular theory, explain why an increase in temperature should be expected to increase the rate of a reaction.
4. By means of equations, give one laboratory method and one commercial method for the preparation of hydrogen.
5. What are the chief large-scale uses of hydrogen?
6. In general terms, distinguish between laboratory and commercial methods for the production of chemical substances.
7. In terms of what happens to the atoms and ions involved, explain clearly the changes that occur when tin and hydrochloric acid (HCl) react to form hydrogen.

8. Summarize the more important chemical properties of hydrogen.
9. List four factors which have a bearing upon the rates at which chemical reactions occur.
10. Justify the view that an increase in the state of subdivision of a solid amounts to an increase in concentration.
11. In addition to the method outlined in this chapter, suggest some other means whereby hydrogen and carbon monoxide might be separated.
12. Given the information that one particular element acts as a catalyst for a certain reaction, and assuming that it is desired to find a better catalyst, what other elements should be investigated first? Why?

COLLATERAL READING

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Oxygen

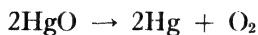
OVER and above its role as the most abundant element in the earth's crust and an element that is essential to all life processes, oxygen is of major importance for still other reasons. The human body is 65 per cent oxygen,¹ and this element is a major component of practically all the different kinds of food consumed by man. Oxygen is essential to the process of combustion of fuels, including those used in motors, heating units, and the human body. For the reason that oxygen is so widely and abundantly distributed throughout terrestrial matter and because of its all-embracing importance, this element is indeed an appropriate one for a somewhat detailed study.

The Discovery of Oxygen. The history of the discovery of oxygen is one of the most revealing chapters in the evolution of the science of chemistry. It is the record of a slow and seemingly painful approach to the true understanding of something that today seems most simple and elementary. Volumes have been written about the many false starts, misdirected efforts, and misinterpreted observations that are intertwined with the laborious but steady accumulation of the knowledge that ultimately led to the recognition of oxygen as an elemental substance.

Most historians of science are agreed that the Englishman Priestley (Fig. 55) and the German Scheele (an apothecary in Sweden) must have discovered oxygen at about the same time and entirely independently. Scheele probably first prepared oxygen in 1771, but Priestley was the first to publish the results of his experiments (in 1774) and is consequently credited with priority in the discovery. Priestley

¹ The three principal component elements that make up the human body and the approximate percentages in which they are present are oxygen (65 per cent), carbon (20 per cent), and hydrogen (10 per cent). The remaining 5 per cent consists of several elements, including calcium, nitrogen, phosphorus, sulfur, sodium, potassium, iron, copper, fluorine, and iodine.

prepared substantially pure oxygen by heating mercuric oxide and thereby decomposing it into mercury and oxygen.



He collected the gas over water and carried out numerous kinds of experiments with this substance (Fig. 56), which he considered to be a

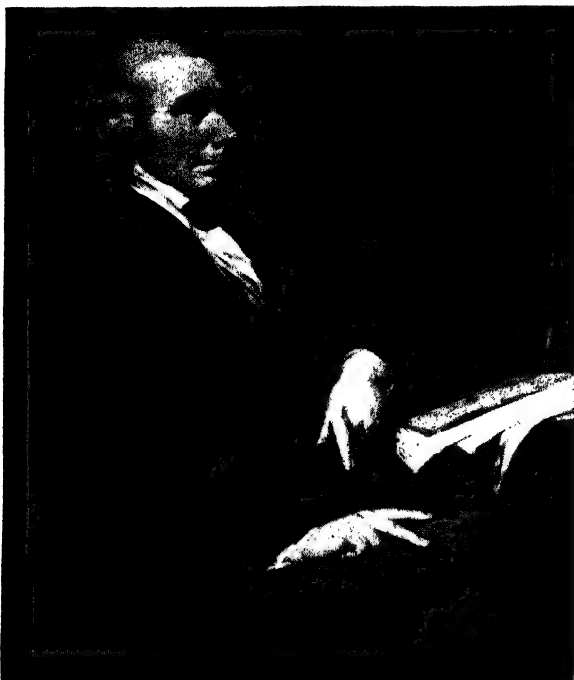


Figure 55. Joseph Priestley. (Courtesy of the Edgar F. Smith Memorial Collection, University of Pennsylvania.)

new kind of "air." He showed that different kinds of substances burned more readily in the new gas than they did in ordinary air, and he tested its physiological action upon mice. In time, he decided to inhale some of the gas himself; the result he described in his book entitled "Experiments and Observations on Different Kinds of Air," which was published in 1774. In part, Priestley wrote as follows:

The feeling of it to my lungs was not sensibly different from that of common air, but I fancied that my breast felt peculiarly light and easy for some time

afterwards. Who can tell but that in time this pure air may become a fashionable article in luxury? Hitherto, only two mice and myself have had the privilege of breathing it.

As noted previously, Priestley came to America and spent the last years of his life at Northumberland, Pa. One hundred years after

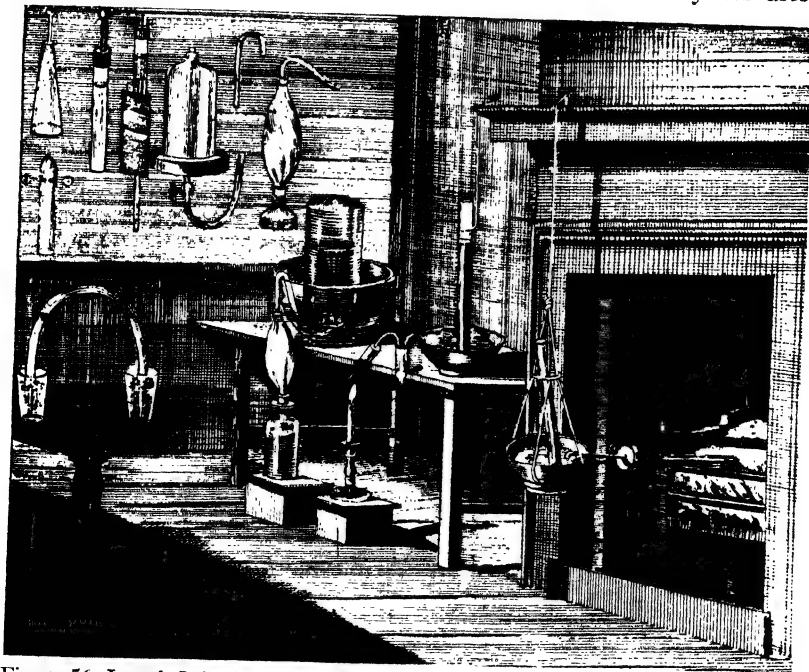
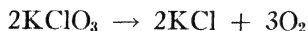


Figure 56. Joseph Priestley's laboratory. (Courtesy of the Edgar F. Smith Memorial Collection, University of Pennsylvania.)

Priestley's discovery of oxygen, a memorial service was held there and was attended by this country's most distinguished scientists. On that occasion also was founded the American Chemical Society, which has grown to be the world's largest organization of scientists, with a membership of more than 60,000.

Preparation of Oxygen. Although oxygen may be prepared in the laboratory by the decomposition of water by means of an electric current, this procedure is not ordinarily used simply because more convenient methods are available. Many but by no means all compounds containing oxygen may be decomposed by the application of heat to

produce oxygen and other decomposition products. Thus, just as Priestley prepared oxygen by heating mercuric oxide, so at present we proceed in a similar manner but use other oxygen compounds. It has become almost traditional that one of the laboratory experiments in the work of the elementary course in chemistry or general science is the preparation of oxygen by the decomposition of potassium chlorate.



It is necessary to heat the potassium chlorate to about 400°C. in order to have oxygen liberated at a feasible rate. If, on the other hand, a little manganese dioxide (MnO_2) is added to serve as a catalyst, a temperature of only 200°C. is required. The catalyst permits the decomposition to occur at about the same rate but at a much lower temperature. One may reasonably inquire whether the oxygen (at 200°) may not come from the MnO_2 rather than the KClO_3 , and to this question there must be found a satisfactory answer based upon experimental fact. The answer is simple. Experiments show that manganese dioxide does not decompose unless it is heated to well above 500°C. Furthermore, after heating KClO_3 and MnO_2 together to produce oxygen, the MnO_2 may readily be recovered unchanged and in the same quantity as was added initially.

Not all compounds of oxygen are suitable for the laboratory-scale preparation of this element. Others that may be used conveniently include mercuric oxide, potassium nitrate (KNO_3), and lead dioxide (PbO_2). Some oxygen compounds when heated give up all of their oxygen, some only a part, and others none at all.

Quite unlike hydrogen, the element oxygen is not usually produced commercially by the decomposition of its compounds. If very pure oxygen is needed, the electrolytic decomposition of water is a satisfactory method but the cost (owing to the electrical-energy requirement) is excessive except to produce comparatively small quantities of oxygen for certain specialized uses. The bulk of the world's commercial supply of oxygen is obtained from the atmosphere.

The Fractional Distillation of Liquid Air. By appropriate application of the principles already discussed in connection with the liquefaction of gases, it is possible to convert "air" from the gaseous to the liquid state. Before the air is liquefied, it is treated chemically so as to remove

water vapor, carbon dioxide, and other minor components so that the air actually liquefied contains only nitrogen, oxygen, and the inert gases.

As a basis for discussion of the physical process whereby these gases are separated, let it be assumed that we have at hand a sample of this liquid air at a temperature of -200°C . and at atmospheric pressure. When the temperature is raised to -195° (the boiling point of liquid nitrogen), the nitrogen boils (evaporates, distills) and the temperature remains at -195° until most of the nitrogen has evaporated. The heat energy supplied at -195° is used in transforming liquid nitrogen to gaseous nitrogen. About four-fifths of the liquid air evaporates at this temperature, and this fraction of the sample is collected separately for sale as nearly pure nitrogen. When practically all of the nitrogen has distilled off, the heat energy being supplied from the surroundings serves to raise the temperature of the remaining liquid up to the boiling point of oxygen, -183°C . At this temperature the oxygen boils off and thus a second fraction, which consists of fairly pure oxygen, is collected separately. This procedure represents a somewhat oversimplified illustration of the process whereby the components of a liquid mixture are distilled off in the respective order of their boiling temperatures and are collected as separate fractions. This procedure is called *fractional distillation*. (See also Chapter 25.)

The preceding illustration, of course, neglects the fate of the inert gases, but it does show how a reasonably good separation of nitrogen and oxygen may be attained. Neither product is of high purity, but both are sufficiently pure for most of the large-scale uses for these elements. It is of interest to note that the nitrogen- and oxygen-gas industries enjoy an unlimited and free supply of raw materials. Some idea of the magnitude of these industrial operations may be gained from the data of Table 5, which lists the production of oxygen in millions of cubic feet for a period of seven years.

These data show clearly the relatively small annual prewar production in 1941, the peak war-stimulated production in 1944, and another upward trend beginning in 1947. The reason for the latter will be given in connection with the discussion of uses for oxygen.

Properties of Oxygen. Solid oxygen has a pale blue color and melts at -218.4°C . As indicated previously, the resulting blue liquid boils at -183°C ., the gas thus formed being colorless, odorless, and tasteless.

TABLE 5. Data on the Production of Oxygen*

Year	Millions of cubic feet
1941	8,682
1942	12,801
1943	16,530
1944	18,495
1945	13,943
1946	10,866
1947	14,000†

* Data from *Chemical and Engineering News*, **25**, 2940 (1947).

† Estimated.

This gas is slightly heavier than air and dissolves in water to only a very limited extent (*ca.* 3 cc. of the gas per 100 ml. of water).

The single oxygen atom does not exist alone except under rather unusual conditions; the normal mode of existence of the element is the diatomic covalent molecule represented by Fig. 57.

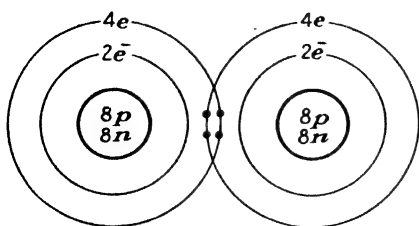
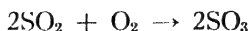


Figure 57. Diagram representing the covalent oxygen molecule. (Shared electrons are represented by black dots.)

Oxygen combines (directly or indirectly) with all elements save the inert gases to form relatively simple compounds known as *oxides*. Thus, the non-metallic element sulfur unites directly with oxygen to form sulfur dioxide,



and this in turn may react with still more oxygen to form sulfur trioxide.



These cases serve also to illustrate that one element may form more than one simple compound with oxygen. In a similar manner the metal zinc combines with oxygen to form zinc oxide.



Combustion. When sulfur, zinc, or other elements, compounds, or mixtures unite with oxygen at a rate such that energy is liberated in the form of heat and light, the process is said to be one of *combustion*.

Actually, combustion is nothing more than a very rapid process of burning. If, for example, a piece of iron wire is heated until it is red-hot (at which temperature it combines slowly with oxygen of the atmosphere) and is then thrust into a bottle containing pure oxygen, the reaction proceeds at a very much greater rate (corresponding to combustion) because the concentration of oxygen molecules in the bottle is much greater than in ordinary air.

Many processes of chemical union with oxygen go on about us all of the time, but at low rates. Many of the common metals corrode or tarnish at different rates, and oxides are formed in the process. The "hardening" of certain kinds of oils (*e.g.*, linseed oil) involves direct union with oxygen, and this is the basis of probably the single most common case of *spontaneous combustion*. When an oil-soaked rag is spread out and exposed to the atmosphere, the heat liberated as a result of the reaction between the oil and atmospheric oxygen is dispersed because of air currents. If, however, the oil-soaked rag is massed so that insulation is provided and the heat of reaction cannot readily be dissipated, the heat accumulates, the temperature rises, and the reaction consequently becomes more and more rapid. Finally, the mass is heated to its so-called *ignition temperature*, and it bursts into flame.

Uses of Oxygen. Large quantities of oxygen are used in the metals industries for cutting and welding operations. In these applications, oxygen together with acetylene or hydrogen is used as a fuel in the oxyacetylene (Fig. 58) or oxyhydrogen torches. Minor uses for oxygen include its medical applications (Fig. 59) in the treatment of ailments such as pneumonia and its use as a mixture with gaseous anesthetics



Figure 58. An oxyacetylene torch in use in cutting through steel plate one and one-half inches thick. (Courtesy of the Linde Air Products Co.)

such as ethylene, C_2H_4 , and nitrous oxide, N_2O ("laughing gas"). This is a rather obvious procedure, since even during the period of anesthesia the patient must have a supply of oxygen sufficient for normal respiratory functions. Cotton soaked in liquid oxygen has

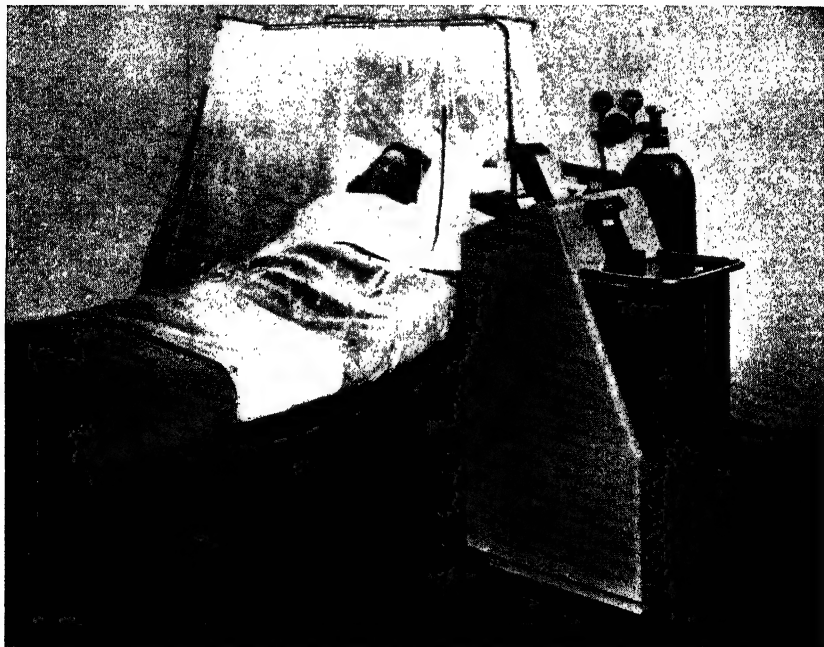


Figure 59. An electrically cooled oxygen tent in use. (Courtesy of the Linde Air Products Co.)

found limited application as an explosive that may be used in place of dynamite.

Oddly enough, one of the factors that operates against expansion of the industrial utilization of oxygen is the high purity of the commercial product. The existing methods for the production of oxygen are such that they provide a product of purity greater than 99 per cent, and these methods are costly. During World War II, experimental work that originated in Russia and Germany and has been extended in the United States and elsewhere has led to great improvements in methods for the production of less pure but much cheaper oxygen. Whereas oxygen once sold for more than \$300 per ton, it now seems likely that

a satisfactory product for some industrial uses may ultimately be had for as little as \$3 per ton.

One of the most promising prospects for an expanded market for oxygen is found in the iron and steel industry. Experiments conducted since World War II show that a substitution of oxygen for ordinary air in the open-hearth furnace (see Chapter 21) leads to savings in time, fuel, and labor costs. Numerous other uses for oxygen in the chemicals-producing industries await developments that will provide oxygen in larger quantities at lower cost. An interesting side light which reflects the manner in which the chemical (and other) industries are economically interrelated is concerned with the inert gases. If oxygen production is greatly expanded, much greater supplies of the inert gases will certainly be produced as by-products, and at lower cost. This will inevitably result in new uses for these gases, and it may not be long before krypton and xenon come into the widespread use heretofore obviated by short supply and high cost.

Ozone. While it is true that the element oxygen normally exists in the form of diatomic molecules, another mode of existence is possible. As early as 1785, Van Marum observed that air in the immediate neighborhood of electrical discharges had an unusual odor. Many years later it was discovered that this odor is due to a form of oxygen represented by the formula O_3 . This substance was given the name *ozone* (from the Greek word meaning *to smell*).

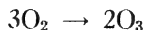
The existence of an *element* in two or more different forms constitutes what is known as *allotropy*, and the specific chemical individuals involved are called allotropic forms or allotropic modifications of the element in question. Many of the chemical elements exhibit allotropy; notable examples are the non-metals sulfur and phosphorus, and the metal tin.

In addition to its occurrence in the atmosphere (Chapter 7) and its unintentional production during the operation of electric generators and the like, ozone is produced commercially by the action of an electric discharge upon air or upon pure oxygen. In either case, only a small portion of the available oxygen is converted to ozone, and the product of these commercial operations is often called "ozonized air."

Under ordinary atmospheric conditions ozone is a gas which has a garlic-like odor so potent that the presence of ozone may be detected by its characteristic odor even when the gas is present at concentrations

as low as one part per ten million parts of air. The "fresh" odor of the air following thunderstorms is largely caused by the presence of ozone. This substance may also exist as a blue liquid and as a violet-colored solid. The gas dissolves in water to an extent about fifteen times as great as ordinary oxygen.

The formation of ozone from oxygen,



is a strongly endothermal reaction. Since so much energy is required for the formation of ozone, it follows that this energy must be stored up in the product of the reaction. Because of its high energy content, ozone is very reactive chemically; some of its reactions occur with explosive violence, particularly when the ozone is present in high concentrations. In general, the reactions of ozone are much like those of oxygen except that they occur at much greater rates. Ozone decomposes readily, and the decomposition product is ordinary oxygen, *i.e.*, the reaction represented by the foregoing equation is reversible.

Ozone has found numerous minor applications, but these have been ones that have required only limited quantities of the gas in low concentrations. Thus it has found application as a bleaching agent, as a germicide, as a deodorant, and in the artificial aging of tobacco, leather, linoleum, and certain food products. Particularly in recent years, expanded production of ozone has resulted from its use in the treatment of municipal water supplies. Used in place of chlorine, ozone eliminates the organic impurities that are responsible for undesirable colors, odors, or taste, and destroys algae and many kinds of microorganisms. With respect to its germicidal properties, ozone is decidedly superior to chlorine.

Progress in the use of ozone in water treatment has come mostly through work initiated in Europe. An ozone plant in Paris provides for the treatment of over 75 million gallons of water per day, and its operation has proved satisfactory. The major experiment in the United States is the huge ozone plant put into operation in Philadelphia in 1948. This plant has a capacity for the production of 1250 lb. of ozone per day, and this is sufficient for the treatment of 36 million gallons of water. Because of the manner in which ozone is produced, the economic

considerations center largely about the cost of the electrical energy required. Ozone plants require little in the way of operating staff or maintenance.

The Naming of Chemical Compounds. To anyone of limited technical background, the names employed by the chemist with reference to specific compounds are at first wholly unintelligible and for a longer time confusing. One may go further and admit also that even the chemist who is well trained and expert in one phase of chemistry may be somewhat less than glib in the use of the nomenclature of some other field of chemistry.

No matter how modest a chemist may be with respect to his own individual accomplishments, it is characteristic that he is intensely proud of the over-all accomplishments of his chosen profession. This pride is amply justified by the facts, but at the same time the chemist should stand equally ready to admit that there are certain areas in which chemists have not done so well. A case in point is the matter of the nomenclature of chemical compounds. When it is considered that there are several hundred thousand known chemical compounds, it seems rather apparent that chemistry should embrace a scheme of nomenclature which is entirely systematic. At best, our present practices in nomenclature may be described as *quasi*-systematic.

Ideally a wholly systematic method for the naming of chemical compounds would be one such that, given the name for the compound, one should be able directly to write the corresponding formula in a manner that would show not only the composition but also the structure, or internal architecture, of the molecule. This is indeed a large order and one that fails utterly to reckon with history. It must be remembered that chemistry grew up more or less haphazardly in its earliest stages. Names were given to substances long before they were recognized as true compounds, and these trivial names became so well established that they have persisted through the years. The result is that, the older the field of chemistry, the less systematic its nomenclature practices are likely to be. Nevertheless, the situation is not really as hopeless as these remarks might suggest.

The following are the formulas and names of a few simple compounds that contain oxygen and that have been mentioned in the preceding pages:

MnO_2	Manganese dioxide
SO_2	Sulfur dioxide
SO_3	Sulfur trioxide
PbO_2	Lead dioxide
Fe_2O_3	Ferric oxide
HgO	Mercuric oxide
H_2O	"Water" (Hydrogen oxide)

From these examples it is seen that these are compounds containing only two kinds of elements (hence, *binary* compounds), and since all of them contain oxygen they are to be classed as oxides. Furthermore, with the single exception of the trivial name, water, these names all end in *-ide*. An additional evidence of regularity of practice is seen in the first four cases, wherein the prefixes *di-* and *tri-* denote the number of atoms of oxygen per atom of the other element. We then come to ferric oxide and mercuric oxide, and these are only typical cases. The suffix *-ic* tells us that there are other oxygen compounds in which there is less oxygen per atom of iron or mercury. There are indeed compounds having the formulas FeO and Hg_2O , and the names of these are ferrous oxide and mercurous oxide, respectively. In these names the suffix *-ous* denotes the relatively lesser oxygen content.

This is all well and good until we go back to the case of lead dioxide and recall, for example, that here, too, there is another oxide of lower oxygen content, that is, PbO , lead monoxide. Why not call these two lead-oxygen compounds plumbic oxide and plumbous oxide, respectively? It would certainly not be entirely incorrect to do so, and these latter names are sometimes used.

It is not the purpose here to embark upon any exhaustive discussion of the nomenclature of inorganic compounds. Rather, it is intended to stimulate an awareness of the magnitude and difficulty of the whole problem of systematic nomenclature. If, as shown by the preceding examples, we are not even consistent in our methods of naming even the simplest of inorganic compounds, how much more involved must be the problem when we are concerned with much more complex substances. There will be occasion later to deal briefly with the systematics of naming a few types of compounds that contain more than two kinds of atoms.

In the study of those chapters which are concerned primarily with organic chemistry, the student will have occasion to see something of more highly systematized practices in nomenclature. Organic chemical nomenclature is more systematic than that employed in inorganic chemistry, for two reasons. First and most important, organic chemistry is a much newer field. The second reason is that organic chemists have been forced to be more systematic literally in self-defense because they have to deal with a vastly larger number of compounds.

In nearly every field of chemistry efforts are presently being made to improve nomenclature practices. This program represents the work of many scientists, and their cooperative efforts are international in scope.

EXERCISES

1. *New terms:* allotropy, binary compounds, combustion, fractional distillation, ignition temperature, oxide, spontaneous combustion.
2. Summarize the commercial uses of oxygen.
3. How is ozone produced? For what purposes is it used?
4. Write equations for two laboratory methods for the preparation of oxygen.
5. List the elements that comprise the human body, and give the percentages of the three major component elements.
6. Outline briefly the principal steps in the process whereby oxygen is produced commercially.
7. In the nomenclature of binary inorganic compounds, what is the significance of each of the following: *-ic*, *-ide*, *-ous*, and Greek prefixes such as *mono-*, *di-*, *tri-*, *tetra-*?
8. In what respects does ozone differ from oxygen? How are the two similar?
9. When MnO_2 is used to catalyze the decomposition of KClO_3 , how do we know that KClO_3 does not catalyze the decomposition of MnO_2 ?
10. Suggest a reason why water vapor must be removed from air before it is liquefied.
11. Suggest a method whereby ozone and oxygen might be separated.

12. Write names for compounds having the formulas CuO , Cu_2O , SiO_2 , ClO_3 , Na_2O .
13. Write formulas corresponding to the following names: magnesium oxide, nitrogen dioxide, uranium trioxide, stannous oxide, stannic oxide.
14. On the basis of the equation for the decomposition of potassium chlorate, (*a*) how many pounds of oxygen can be liberated by completely decomposing 80 lb. of potassium chlorate? (*b*) How many pounds of potassium chloride (KCl) would be formed at the same time?
15. How many tons of air are required to produce one ton of oxygen if the process used is 100 per cent efficient?

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Water

LIKE many another substance that we use extensively from day to day and have come to take for granted, the significance of water as it is used in the home, in agriculture, and in industry is obscured by our very familiarity with this particular compound. Water occurs in, on, and above the surface of the earth in tremendous quantities and in varying degrees of purity. The human body is about two-thirds water, and there are numerous plants, fruits, and vegetables that contain as much as 90 per cent water.

It is a familiar fact that the climatic features and the agricultural utility of the various geographical regions in this or any other country are in large measure dependent upon the annual supply and distribution of rainfall. Man has to some extent been able to substitute, through irrigation, existing terrestrial water supplies in some regions that have an annual rainfall too low or too poorly distributed throughout the year for normal agricultural needs. Thus, water transforms deserts into productive agricultural areas, increases our supplies of foods, and has a profound influence upon our national economy.

In addition to its use in industry as a raw material for chemical and other processes, this substance is used extensively as a heat-transfer or heat-exchange medium. This application may be illustrated most simply by the familiar double boiler (Fig. 60) used in the home. Food to be cooked is placed in the upper container, and water is boiled in the bottom one. The heat taken up by the water in its transfer from the liquid to the gaseous state is imparted to the bottom of the upper container when the steam condenses (changes back from the gaseous to the liquid state). In this manner heat is supplied to the contents of the upper container at a uniform rate and a constant temperature so that the food does not burn as the result of "superheating." There are many similar applications such as the use of water in automobile

radiators to transfer heat from the motor to the surrounding atmosphere, in the cooling of gas streams in the "condensers" used in distillation equipment, etc.

Physical and Chemical Properties of Water. Some of the more important physical properties of water have already been mentioned, *e.g.*, its melting point, boiling point, and temperature of maximum density. The physical properties of water are of greater significance than those of any other single substance because of the extent to which they serve as reference points in thermometry and the establish-

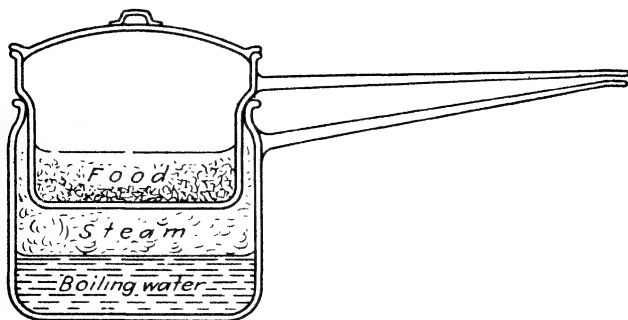


Figure 60. A double boiler.

ment of units of measurement of weight and volume (*vide supra*). The *gallon*, as still another example, is defined as the volume occupied by 8.3378 lb. of water at 62°F. and a barometric pressure equivalent to 30 inches of mercury.

Among other physical properties of all pure liquids that were not discussed in Chapter 9 but that are of especial interest in connection with liquid water are the *specific heat* and the *heat of vaporization*. Again, these are characteristic properties in terms of which liquids may be identified, but they are less readily measurable than some of the other properties of pure liquids. The specific heat of any substance (solid, liquid, or gas) is the quantity of heat required to raise the temperature of one gram of the substance through 1°C. The specific heat of *liquid* water is 1 cal. per gram. The heat of vaporization is the quantity of heat required to change one gram of a liquid to the corresponding gas at the boiling point of the liquid (at atmospheric pressure). The heat of vaporization of liquid water is 540 cal. per gram.

Water is an unusual liquid in that its specific heat and its heat of

vaporization are abnormally high. If one sets out to heat one quart of water from room temperature to the boiling point and then to evaporate this quantity of liquid, the total heat requirement amounts to approximately 532,000 calories. Not only is much heat energy required to raise the temperature to the boiling point, but still larger quantities are required to accomplish the transfer from the liquid to the gaseous state. Thus the old saying that "a watched pot never boils" seems to have some basis.

Like many of the simple binary compounds containing oxygen, water may be formed by the direct union of the two elements. Below 400°C . the reaction between hydrogen and oxygen is slow; above 600° the rate of combination becomes very rapid, and the reaction may occur with explosive violence if the gaseous mixture contains 5 to 70 per cent hydrogen. Whatever the conditions of formation may be, the union of the two atoms of hydrogen with the one of oxygen occurs by virtue of a sharing of electrons, as shown in Fig. 61. In this manner the hydrogen atom achieves the inert helium structure (two electrons in the first shell), while the oxygen atom becomes like neon (eight electrons in the second shell).

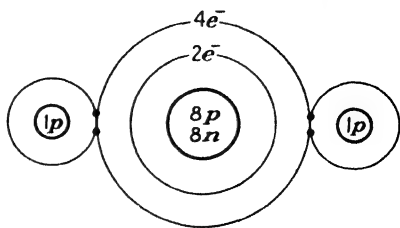


Figure 61. Diagram representing the covalent water molecule. (Shared electrons are shown as black dots.)

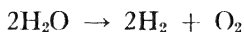
In addition to its formation by direct union of the elements, water is formed as a by-product of very many different chemical reactions including, for example, those involved in the burning of solid, liquid, and gaseous fuels. This point will not be expatiated upon here; the student will come to see how commonly water appears as one of the products of reactions that will be represented by appropriate equations. As a matter of fact, there is little reason to pay much attention to methods for the preparation of water. This substance is so readily available that the chemist seldom has occasion to prepare it; the more typical problem is that of purifying existing supplies of water.

Another notable property of water is the fact that so many substances (solids, liquids, and gases) dissolve in water. For this reason, water is the medium in which the chemist brings together other sub-

stances for the purpose of permitting them to enter into chemical reactions. Because this is such a common practice we are prone to underestimate or overlook completely the fact that water serves to initiate and to catalyze very many different kinds of chemical reactions.

Frequent reference has been made to the electrolytic decomposition of water to provide hydrogen and oxygen. It is not a very satisfactory

procedure simply to decompose pure water by the action of a direct current, for the reason that water is a very poor conductor of electricity. That is, pure water offers too great resistance to the passage of the electric current. This difficulty may be obviated by dissolving in the water a little H_2SO_4 , for example, which decreases the electrical resistance without altering the end result of the process. In the laboratory, this reaction



may be carried out conveniently in an apparatus of the type shown in Fig. 62, so that the hydrogen and oxygen may be collected separately.

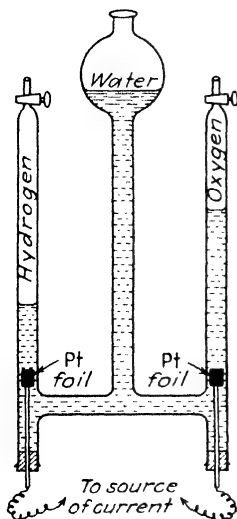


Figure 62. Decomposition of water by electrolysis. Note that the reaction provides twice as much hydrogen as oxygen.

Ionization. For the reason that water is so commonly used as the medium in which to dissolve other substances and that in which so many chemical reactions are carried out, it seems appropriate to use water as the basis for discussions which will clarify certain questions which should be raised relative to the discussion of the

electrolytic decomposition of water. Among other questions that ought to be raised are the following: Why is pure water a poor conductor of electricity? Why is water containing H_2SO_4 a better conductor than pure water? Answers to these and several related questions may be had by inquiring into the condition in which dissolved substances exist in water. It should be clearly understood that water is being used as an illustration because it is by far the most important but by no means the only solvent in which solutes ionize.

In the following discussion three new terms are needed. It is necessary to recognize that the addition of a substance such as H_2SO_4 to

water results in a homogeneous mixture known as a *solution*. The added substance (in this case, H_2SO_4) is called the *solute*, and the substance in which the solute is dissolved is called the *solvent*. The ability of water to dissolve other substances (*i.e.*, to act as a solvent toward them) is so great that water is often referred to as the nearest approach to a universal solvent. The terms solute, solvent, and solution will be treated in more detail in the next chapter.

Still further, we must know that the different forms of matter may be classified in terms of their ability to act as conductors of electricity. Everyone knows that certain metals (*e.g.*, copper) in the form of wire are used to conduct electricity without undergoing change in the process. That is, a wire may be used almost indefinitely as a conductor, and so far as we can tell the wire is thereafter no different because of the experience. We may consider that the passage of current through the wire consists of a flow of electrons and that this does not bring about any chemical changes in the metal. On the other hand, there are many substances that conduct electricity (*e.g.*, solutions), but they do so only by virtue of the occurrence of chemical changes. Such substances are called *electrolytes* and may be further classified in a very rough manner as *weak electrolytes* and *strong electrolytes*. It is to be inferred that solutions of weak electrolytes in a solvent such as water are poor conductors of electricity, whereas just the opposite is true of solutions of strong electrolytes.

Weak Electrolytes. It should not occasion much surprise when it is pointed out that the conduction of electricity by solutions is dependent upon the presence in the solution of those electrically charged species called ions (Chapter 5). In accordance with earlier discussions of modes of compound formation we know that some compounds are formed at least largely by the sharing of electrons, and hence the act of chemical union does not give rise to ions. For example, one would visualize the formation of mercuric chloride, HgCl_2 ("bichloride of mercury") as involving the sharing of electrons between a mercury atom (periodic table, Group II) and two chlorine atoms (periodic table, Group VII). The resulting molecule is largely covalent, and one would therefore expect it to be a weak electrolyte. One might indeed expect it to be a non-electrolyte, but it is found by experiment that this substance does dissolve in water to form a solution which is a conductor of electricity, albeit a poor one.

Explanation of the conductance of electricity by solutions of weak electrolytes rests upon a theory enunciated by the Swedish chemist Svante Arrhenius (1859–1927) in the year 1887. In terms of this theory we should interpret the behavior of mercuric chloride, for example, as follows: When the HgCl_2 molecules are dissolved in water and come under the influence of the solvent molecules, the HgCl_2 actually separates into ions, but to only a small extent.



This process is called *ionization*, and the mercuric chloride molecules are said to *ionize*. The use of the two arrows in the ionization equation shows that it is a reversible process and that this constitutes still another example of dynamic equilibrium. A solution of mercuric chloride in water contains many un-ionized HgCl_2 molecules but only a relatively small number of Hg^{++} and Cl^- ions. Because so few ions are present to act as carriers of the electric current, the solution is a poor conductor and the solute is classed as a weak electrolyte.

With reference to the question as to why water is a poor conductor of electricity, one must recall that the water molecule is highly covalent. From this fact one may infer that the ionization of water,



occurs to only a very slight extent. Such is the case. Water is not only a weak electrolyte, but a very weak one. The reason for the increased ability of a water solution of H_2SO_4 to conduct the current now becomes rather apparent. It is due to the fact that, in water solution, H_2SO_4 exists in the form of ions to an extent sufficient to account for the increased electrical conductivity.

Strong Electrolytes. The ideas employed in the discussion of weak electrolytes are of little value in connection with those substances which are formed by loss and gain of electrons. It has been shown that sodium chloride is formed owing to the loss of an electron by the sodium atom and the gain of this electron by the chlorine atom (Chapter 5). Thus two *ions* are formed, and the formula for sodium chloride should be written, Na^+Cl^- . Now if solid sodium chloride already consists of ions, we may not argue that ions arise when this solute is dissolved in water. One might be tempted to conclude that all such

ionic solutes are very strong electrolytes, but this conclusion is not entirely warranted. In a solution of Na^+Cl^- in water, there are so very many ions that those of one charge interfere (by electrostatic attraction) with the ability of those of opposite charge to act as conductors of the current. The net result is that, whereas compounds formed by loss and gain of electrons are strong electrolytes, their solutions are not so good conductors as one would expect unless there is so little solute in the solution that the interference is minimized.

The behavior of strong electrolytes is explained in terms of the Debye-Hückel theory, which need not be elaborated here. It should be understood, however, that a proper interpretation of some of the properties of both weak and strong electrolytes requires a much more extensive study of chemistry than is possible in a first course. It is worth while also to note how an understanding of the structure of atoms and the various modes of compound formation is useful in arriving at an understanding of the process of conduction of electricity by solutions of electrolytes. Here again it is seen by what intricate processes the problems of science are solved. At one time it was thought that the theory of Arrhenius applied equally well to all electrolytes. However, new knowledge arising from the study of the structure of crystalline solids showed that this theory would not serve to explain the properties of what we now call strong electrolytes. This particular instance is no exception but rather a more or less typical case. We have come to realize that any isolated fragment of information may one day be used in some wholly unanticipated way to arrive at a better understanding of some phenomenon quite foreign to the thinking which led to the discovery of the original and apparently isolated fact.

The student may well wonder what all of this has to do with water, except for the fact that water is the liquid medium in which most ionization processes occur. Actually, it is necessary to know something of the manner in which solutes exist in water before the subject of water purification may be studied most profitably.

The Purification of Water. From the outset it should be clearly appreciated that methods of purification and their attendant effectiveness are inevitably related to the purpose for which the substance in question is to be used. A given method may provide water that is pure enough for some uses, and yet this same water would be con-

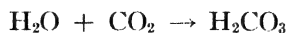
sidered grossly impure in relation to certain other uses. Accordingly, it is necessary to consider methods of purification in terms of intended applications. In any event, the term *purification* implies the separation of a given substance from all other kinds of atoms, molecules, or ions, and the efficiency of the method is gauged in terms of the extent to which this objective is realized. The treatment of water with various chemicals for the purpose of killing bacteria is in a sense one phase of water purification. Any detailed discussion of this aspect of the problem is beyond the scope of this book.

Purification of Water by Distillation. For use in the laboratory and for certain specialized commercial uses it is often necessary to provide water of very high purity. This presents a peculiarly difficult problem because water is such an excellent solvent that it will pick up impurities when it comes into contact with the very vessels employed in the purification process. In order to produce water of maximum purity one starts with the purest water available, and this is usually water which has had treatment equivalent to that normally given to municipal water supplies. In such partially purified water there are very few impurities (and these in very small quantities) that have an appreciable vapor pressure, and this fact alone suggests the use of a process of distillation.

The purification of water by distillation on a laboratory scale may be accomplished by the use of an apparatus such as that shown in Fig. 63. The impure water in the flask is boiled by heating it with an ordinary burner flame. The resulting steam passes upward through a distillation tube bearing a thermometer (which permits one to observe the boiling point) and thence into the water-cooled "condenser." Upon coming into contact with the cool wall of the inner tube of the condenser, the steam condenses to liquid water, which is collected in a suitable vessel. To produce water of ultimate purity, redistillation and the incorporation of a number of refinements in the equipment and procedure are necessary.

The Origin of Impurities in Natural Waters. Natural water supplies are derived either directly or indirectly from the oceans. Oceanic waters evaporate (leaving behind the solids that were either dissolved or suspended therein), condense in the atmosphere under appropriate conditions, and fall to the earth as rain. Thereafter, the water is available from the rivers, lakes, and springs. During rainfall or while natural

waters are exposed to the atmosphere, some of the carbon dioxide of the atmosphere dissolves in the water and forms solutions of carbonic acid.



These slightly acid solutions come into contact and react with rocks, clays, and other solids to form compounds that dissolve in the water.

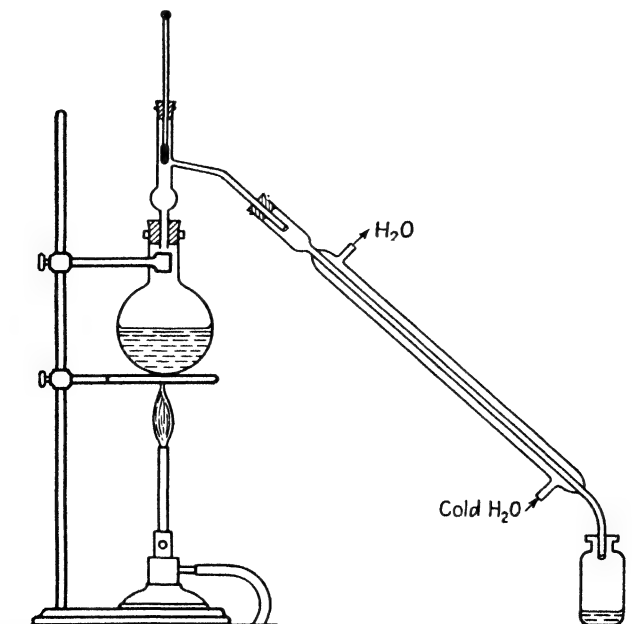
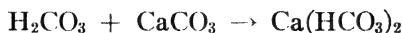


Figure 63. Apparatus for the purification of water by distillation.

Thus water containing even a small amount of carbonic acid will react with ordinary limestone (principally calcium carbonate, CaCO_3) to form calcium hydrogen carbonate.



In similar fashion natural waters come to contain compounds made up principally of calcium (Ca^{++}), magnesium (Mg^{++}), hydrogen carbonate (HCO_3^-), chloride (Cl^-), and sulfate (SO_4^{--}) ions. The presence of these ions constitutes the property of "hardness" of natural waters.

In addition, natural waters contain suspended solid matter (both inorganic and organic) and dissolved impurities arising from pollution

by industrial, agricultural, and animal wastes, from sewage-disposal plants, etc. These impurities are so many and so diverse in their origin that it is useless to attempt to indicate any normal or average level of impurities. Suffice it to say that any problem of natural water purification must necessarily be approached only after a careful examination of the water supply to determine both the nature and the quantity of the various impurities to be removed.

The Historical and Economic Aspects of Water Treatment. The desirability of treating natural waters in a manner designed to render them more palatable and safe for human consumption is certainly no recent development. Ancient man recognized that muddy river water was unattractive and that it became less so when the suspended solids were allowed to settle out. There is ample reason to believe that primitive man associated great healing and purifying powers with heat and fire, and the practice of making water more suitable for use by the simple expedient of boiling it is undoubtedly a very old one. The recognition of some relationship between water pollution and the incidence of disease must have come quite early; this is clearly demonstrated by the following early English edict issued in the year 1612 and relating to the waters of the New river which provided part of the water supply for the city of London:

Wee doe by these presents for us our heirs and Successors straightly charge and Comaund all pson and psons whatsoever That they or anie of them doe not hereafter cast or putt into the said new river anie earth rubbish soyle gravell stones dogges Catts or anie Cattle Carrion or anie unwholesome or uncleane thing nor shall wash nor clense anie clothes wooll or other thinge in the said river . . . nor shall make or convey anie sincke, ditch Tanhowse dying howse or seege into the said river or to have anie fall into the same.¹

One of the earlier practices in water treatment was that of simple filtration through finely divided sand. This served to remove most of the suspended solids as well as many of the bacteria and much of the nitrogen-containing organic matter. This procedure is, of course, ineffective in the removal of those impurities which are dissolved in the water. Natural waters from springs are clear because they have experienced repeated filtration through underground sands, but such waters are usually of very high mineral content.

¹ Reproduced from the "Encyclopaedia Britannica," by permission of Walter Yust, Editor.

Over and above considerations that relate directly to water purity and water-borne diseases, the large-scale treatment of water supplies is motivated to a considerable degree by purely economic factors. Savings amounting to millions of dollars per year are achieved simply by removing calcium and magnesium ions from natural waters. These ions, if allowed to remain in water used for laundering operations, react with soap and form insoluble curdy solids. One may realize no cleansing action from the soap until after enough has been added to remove the calcium and magnesium ions. The ring around the bathtub is both unattractive and uneconomical.



Figure 64. A pipe containing a heavy deposit of "boiler scale." (Courtesy of The Permutit Company.)

Quite apart from the waste of soap owing to the presence of calcium and magnesium ions is an economic factor that is related to the presence of hydrogen carbonate (bicarbonate) ions in natural waters. When waters containing, for example, magnesium and bicarbonate ions are heated, the dissolved ions are converted to a solid.

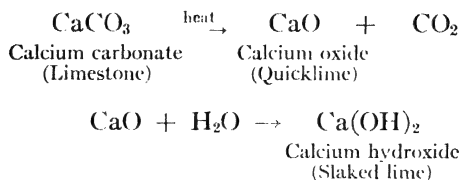


In steam boilers, hot-water pipes, steam radiators, and the like, these solids (e.g., magnesium carbonate, MgCO_3) deposit as an incrustation known as *boiler scale* (Fig. 64). If much solid deposits in this manner, the efficiency of heat transfer is greatly diminished. In extreme cases, pipes become completely clogged, and this leads to either destructive explosions or the need for costly replacement of equipment, or both.

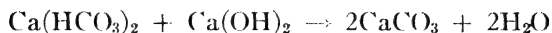
The Removal of Temporary Hardness from Natural Waters. In natural waters, *temporary hardness* is that resulting from the presence of the

bicarbonates of calcium, magnesium, and (in some localities) iron. The term temporary hardness is used because of the relative ease of removal of these impurities. As indicated in connection with the discussion of the deposition of boiler scale, these bicarbonates are converted to carbonates merely by boiling the water. Thereafter, the solid carbonates may be removed by filtration. This procedure is wholly impractical for large-scale operation because of the prohibitive cost of the heat energy necessary to boil millions of gallons of water.

The procedure usually employed was first used in municipal water plants about 1912. The process involves the addition of "slaked lime," which is produced from limestone (or materials of similar composition) by the following sequence of reactions:

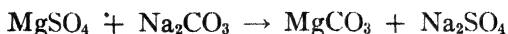


Addition of slaked lime to the water results in the separation of solid carbonates of calcium, magnesium, etc.



The resulting solid carbonates settle out, and in so doing they carry down with them some of the suspended solids already present in the water. If slaked lime is added somewhat in excess of the need illustrated by the foregoing equation, a pronounced bactericidal action is also achieved.

The Removal of Permanent Hardness from Natural Waters. Because these impurities are more difficult to remove, the chlorides and sulfates of calcium and magnesium (that is, CaCl_2 , MgCl_2 , CaSO_4 , MgSO_4) are said to constitute *permanent hardness*. The removal of these constituents is accomplished by the addition of sodium carbonate, Na_2CO_3 (usually in the form of the commercial product called *soda ash*). Here again, the magnesium and calcium chlorides and sulfates that are dissolved in the water are converted to the corresponding solid carbonates.



The Simultaneous Removal of Temporary and Permanent Hardness. In practice, both temporary and permanent hardness are removed at the same time by the addition of slaked lime and soda ash. This is the so-called *lime-soda process*. Other chemicals (something of the order of a dozen in all) are added for specific purposes where needed. The lime-soda process is both inexpensive and reasonably effective but does not do a complete job of "softening" the water. This is not entirely disadvantageous because the complete removal of dissolved substances from water for human consumption is not desired. Pure distilled water has a "flat" taste and is therefore quite unpalatable.

A relatively modern practice in water treatment employs naturally occurring or artificially prepared substances classed as *zeolites*. These procedures are sometimes called "ion-exchange processes" because of the manner in which they function to remove hardness (both temporary and permanent). The zeolites are very complex inorganic substances belonging to the class of compounds called *silicates*. For purposes of simplification, a sodium zeolite, for example, may be represented by the formula Na_2^+Z^- , where Z represents the complex negative zeolithic ion. When hard water comes into contact with a bed of solid granular sodium zeolite (Fig. 65), the calcium and magnesium ions are exchanged for sodium ions.



The useful life of a zeolite bed ends, of course, when all of the sodium ions in the original solid zeolite are replaced by calcium and magnesium ions. The zeolite may however be "regenerated" (restored to its original condition) quite simply by passing over it a concentrated solution of ordinary salt. This is an application of the mass law, wherein the calcium and magnesium zeolite is contacted with a solution containing so many sodium ions that the Ca^{++} and Mg^{++} are replaced by Na^+ and the processes represented by the foregoing equations are reversed. The zeolite is then ready to use again; and if the bed is regenerated in this manner at suitable intervals, the zeolite may be used almost indefinitely.

Zeolite water-softening units are gaining in popularity for use both

in industry and in the home. Artificial zeolites that provide for the removal of negative as well as positive ions are now available, and they soften water so efficiently that they are being substituted in places where water was formerly purified by distillation.

Mass Medication via Public Water Supplies. The use of chemical treatment to soften water or to make it more palatable is an accepted practice. In addition, a marked decrease in the incidence of water-

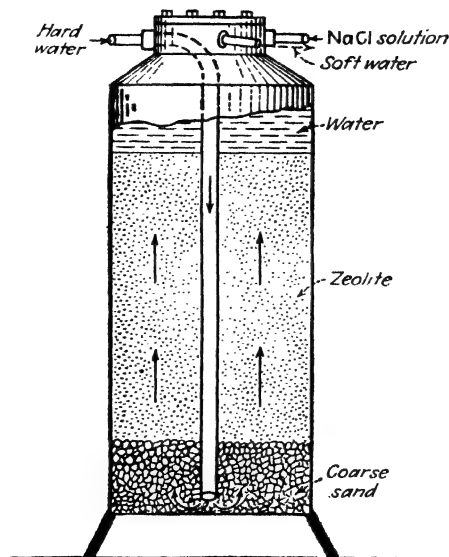


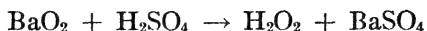
Figure 65. Purification of water by the use of a zeolite.

borne diseases resulting from the use of chlorine, ozone, and similar chemicals to destroy harmful bacteria has certainly been amply demonstrated. These practices naturally lead to the question as to whether it might not be feasible and desirable to enter upon a program of mass medication of populations by the addition of appropriate medicinal chemicals to public water supplies. This question entails both scientific and sociological considerations. A real element of responsibility is self-evident when one considers the possible results of errors that might occur. Cost factors also loom large when one remembers that only a small fraction of the water treated in municipal water plants is used for human consumption.

At various times in the past, iodine (in the form of iodides such as

NaI) have been added to public water supplies for the purpose of preventing goiter. This was done on a purely experimental basis, and the experiments were usually short-lived. More recently, there has been considerable agitation for the addition of fluorides (e.g., NaF) to public water supplies as a means of preventing or minimizing dental caries (tooth decay). It seems well established that there is a good correlation between the incidence of dental caries and the fluoride content of the water taken into the body. In several cities in the United States, experiments are being conducted on a mass-population basis to determine the feasibility of adoption of the practice of fortifying public water supplies with fluorides. The over-all problem, however, is not a simple one. It must be determined, for example, whether added fluorides will serve as well as those naturally present in water supplies in certain localities. Further, it must be remembered that too much fluoride causes an unattractive mottling of the dental enamel. Curiously enough, the most vehement demands for this type of medication come from the public, and these demands are usually based upon incomplete or misleading information. The medical, dental, and other interested professions generally follow a more conservative course which requires that decisions be reached only after entirely conclusive *experimental evidence* has been accumulated. In any case it seems clearly evident that the possibly deleterious effects of such practices must be evaluated carefully in relation to the potential gains in the form of a generally improved public health.

Hydrogen Peroxide. In Chapter 3 it was indicated that the elements hydrogen and oxygen may combine so as to form a compound other than water, *i.e.*, hydrogen peroxide, H_2O_2 . This compound however is not produced by direct union of the elements but rather from commercially available compounds that are closely related to hydrogen peroxide. It may be prepared conveniently by the action of sulfuric acid solution upon barium peroxide.



The solid by-product barium sulfate, BaSO_4 , is removed by filtration, and the solution of hydrogen peroxide in water remains. In large-scale commercial production, hydrogen peroxide is made by an electrolytic process.

Hydrogen peroxide is an unstable colorless liquid that decomposes to form water and oxygen.



This reaction is catalyzed by many different kinds of chemical substances, notably the metals. Because it is also catalyzed by light, solutions of hydrogen peroxide in water are usually stored in brown bottles. A further means of stabilizing the peroxide solution is the use of an inhibitor such as the organic compound acetanilide.

Uses of Hydrogen Peroxide. Most if not all of the practical applications of hydrogen peroxide are based upon its ease of decomposition to produce oxygen gas, together with the fact that the decomposition reaction gives water as the only other product. The medicinal uses are perhaps the most familiar, and for these purposes (gargles, antiseptics, etc.) it is sold by the druggist as a 3 per cent solution in water. While it is certainly true that this compound has a limited ability to kill bacteria, this bactericidal action has been grossly overestimated. Apparently the user is overimpressed by the evidence of action, which is merely the effervescent liberation of gaseous oxygen resulting from the catalyzed decomposition reaction.

Hydrogen peroxide or compounds derived from it are used extensively as catalysts for several different types of reactions. More specifically, this catalytic action is utilized in the formation of certain plastics, resins, and synthetic rubber-like materials. Because of its very mild bleaching action, hydrogen peroxide is used to bleach delicate fabrics such as silk and materials such as bone, ivory, and feathers, and misused to bleach human hair.

During World War II, hydrogen peroxide was used extensively (particularly in Germany) as a propulsion agent. It was used to launch V-1 rocket bombs, to drive the fuel pumps in V-2 bombs, and to propel torpedoes, submarines, and even airplanes. It seems likely that this type of application will be greatly extended in the future unless still more suitable materials are found.

EXERCISES

1. *New terms:* permanent hardness, heat of vaporization, weak electrolyte, solute, ionization, zeolite, solution, temporary hardness, electrolyte, specific heat, solvent, strong electrolyte.

2. Explain how natural waters acquire the property of hardness.
3. Why are weak electrolytes poor conductors of electricity?
4. Explain how water is used as a heat-transfer agent.
5. List the important uses for hydrogen peroxide.
6. Why is it profitable to remove hardness from natural waters?
7. What is (a) "slaked lime"; (b) "quicklime"?
8. What determines the selection of a process for the purification of water?
9. What is meant when we say that a substance ionizes?
10. In what respect are the physical properties of water more important than those of any other liquid?
11. What problem would arise if someone should discover a truly "universal solvent"?
12. Why does the Arrhenius theory not serve in the interpretation of the behavior of strong electrolytes?
13. If, in the use of zeolite water softeners, calcium and magnesium ions replace sodium ions, how may one explain the fact that just the reverse occurs during the zeolite regeneration process?
14. Write equations showing (a) the preparation of hydrogen peroxide and (b) the decomposition of hydrogen peroxide.
15. Write equations that illustrate (a) the removal of temporary hardness from water and (b) the removal of permanent hardness.

COLLATERAL READING

- ELDER, SCOTT, and KANDA: "Textbook of Chemistry," Harper & Brothers, New York, 1948, Chapter 20.
- RAY: "General Chemistry," J. B. Lippincott Company, Philadelphia, 1947, Chapter 11.
- RICHARDSON and SCARLETT: "General College Chemistry," Henry Holt and Company, Inc., New York, 1947, Chapter 13.

Solutions

PROBABLY one of the most popular misconceptions of a technical process is concerned with what happens when a solid dissolves in a liquid. When ordinary sugar is added to hot coffee or tea, the housewife says that the sugar "melts." It does not melt; it dissolves. The melting point of sugar is $186^{\circ}\text{C}.$, and it is patently obvious that this substance could scarcely melt at the temperature of boiling water. The act of melting is usually associated with and is a definite property of pure solids; in the foregoing instance we are concerned with the act of dissolving a solid in a liquid that is capable of acting as a solvent.

This case, however, is a familiar example of the formation of a solution. There are very many other common materials that consist of solutions, *e.g.*, tap water, tincture of iodine (a solution of iodine in alcohol), alcoholic beverages (solutions of alcohol— together with other solutes—in water), household ammonia (a solution of ammonia in water), and many others.

An exploration of some of the more elementary aspects of solutions and their properties is essential to a further study of the nature of chemical changes that take place in solutions. At the same time, a knowledge of the properties of solutions enables one to interpret more intelligently a number of very routine problems. One should at least come to know, for example, what kind of antifreeze is best to buy for the family automobile and why one might need to use these same products during hot summer weather.

Types of Solutions. In Chapter 12 the terms solute, solvent, and solution were defined, but a clear distinction between solute and solvent was not made. Since every solution must consist of at least two components, it is convenient to consider the solute to be that present in the smaller quantity. If 10 g. of alcohol were dissolved in 100 g. of

water, then the alcohol would be looked upon as the solute and the water the solvent. Their roles would be reversed, however, if 10 g. of water were dissolved in 100 g. of alcohol.

At the outset, particular emphasis should be placed upon the status of solutions as *mixtures*, and it should be understood that solutions constitute a special class of mixtures. One may mix sugar and salt in any desired proportions, but one may not dissolve unlimited quantities of salt (or sugar) in a given quantity of water. Thus the composition of a solution may be varied, but only within well-defined limits. The quantity of salt that can be dissolved in 100 g. of water, for example, to form a true solution varies from zero up to the number of grams that represents the maximum possible quantity that will dissolve in 100 g. of water at the prevailing temperature. Still another characteristic of this special variety of mixture known as solutions is the property of homogeneity; a true solution appears homogeneous, regardless of the nature of the solute and solvent.

On the basis of these criteria, *a solution may be defined as a homogeneous mixture the composition of which may be varied only between certain fixed limits.*

While it is certainly true that most of the solutions which one uses from day to day are solutions of solids in liquids, there are as many possible types as there are different combinations of the three states of matter. That is, one may produce solutions of

Gases in liquids	Gases in gases	Gases in solids
Liquids in liquids	Liquids in gases	Liquids in solids
Solids in liquids	Solids in gases	Solids in solids

Solutions in which a liquid is the solvent and the solute is a gas, a liquid, or a solid are very common, and several examples have already been cited. The atmosphere is a good example of a solution in which a gas (nitrogen) is looked upon as the solvent, and oxygen, helium, neon, etc., are all considered to be solutes. Of the remaining types, solutions of solids in solids are the most common, and these are encountered most often among the various alloys of the metals.

Of all the liquid solvents used in the laboratory, in industry, and in the home, water is by all odds that most commonly utilized. Water is the best of the inorganic solvents. The alcohols and numerous other

types of compound are classified as organic solvents (Chapters 26 and 27), and these are of the sort employed as "dry cleaners," nail-polish removers, etc.

Solubility. Up to this point it has been sufficient to think of solutions in more or less general terms. The question of solute-solvent relationships must, however, come to be looked upon in a more precise manner, *i.e.*, one must think of solutions in terms of quantities of solute and solvent. This gives rise to the need for some additional

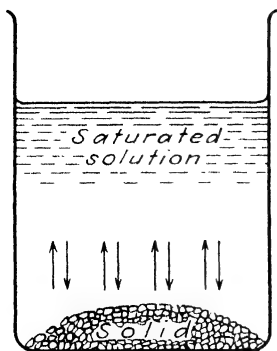


Figure 66. A condition of equilibrium exists between a saturated solution and undissolved solute.

terminology that will facilitate the specification of these relationships. In the discussions which follow immediately it will be assumed that the solutions under consideration are (unless specified otherwise) at room temperature and atmospheric pressure.

The extent to which a given solute will dissolve in any solvent is referred to as the *solubility* of the solute. Accordingly, solubility is defined as the maximum quantity of solute that will dissolve to form a stable solution in a given quantity of solvent at any specified temperature and pressure. When the solvent contains this maximum quantity of solute, the resulting solution is said to

be *saturated*. If, for example, we should add ordinary sodium chloride to 100 g. of pure water at 25°C. until no more would dissolve and an excess of the solid salt were present, it would be found that the solution contained exactly 35.92 g. of NaCl. Thus the solubility is said to be 35.92 g. NaCl per 100 g. of water at 25°, and this is a saturated solution.

What has been said about the act of dissolving should not lead one to infer that a static condition prevails when a saturated solution has been achieved. If any excess solute is present, a dynamic equilibrium exists between the dissolved and undissolved solute (Fig. 66). The molecules (or atoms or ions) of the solute continue to dissolve, and at the same time molecules of the solute leave the solution and redeposit on the solid excess solute. Equilibrium exists when these two processes go on at the same rate, and this state of affairs is entirely analogous to the equilibrium between a liquid and its vapor in a closed container. Accordingly, it is possible to define a saturated solution more precisely

as one that is in equilibrium with an excess of the solute. There are numerous ways in which it may be proved that this condition of equilibrium exists; one of these is a simple and yet very convincing experiment. Let us suppose that we have a saturated solution of a certain solute and a supply of crystals of the same solid solute. Let us suppose also that this solid crystallizes in the form of cubes. If, now, one selects an imperfect crystal (for example, one with a corner knocked off), places this crystal in the saturated solution, and allows it to stand, in time the imperfection in the crystal will be repaired; the crystal will become a perfect cube. This can happen only if there is a continual interchange of solute between the solid and the solution. At equilibrium, solute dissolves from all surfaces of the crystal but redeposits only over the area of the crystal imperfection until it is repaired. This behavior not only proves the existence of a condition of dynamic equilibrium but also provides evidence of the reproducibility of crystal form.

The Dependence of Solubility upon Experimental Conditions. The fact that the preceding discussion was arbitrarily limited to room temperature and atmospheric pressure suggests that both temperature and pressure influence the extent to which solutes dissolve in solvents. In Chapter 7, it was shown how (in accordance with Henry's law) the solubility of gases in liquids is influenced by pressure. Because it is of major importance only with reference to the solubility of gases, pressure will not be considered further in the present discussion. Consideration must be given, however, to the effect of other variables, particularly in relation to the solubility of solutes in liquid solvents.

Whether conscious of it or not, most of us have seen experimental evidence that the solubility of a gas in a liquid decreases with increase in temperature. When a cold bottle of soda water (containing carbon dioxide gas dissolved in water), is opened and allowed to warm up toward room temperature, a persistent evolution of gas bubbles is observed. This means that the gas is less soluble at the progressively higher temperatures and thus comes out of solution in the form of gas bubbles. In general, this behavior is typical of solutions of gases in liquids. A word of caution is not out of place here with reference to a practice that is all too common. If bottles of soda water are placed inside of or in contact with the freezing unit of a household refrigerator, the temperature is often low enough to freeze the liquid contents of

the bottles. Because the solubility of carbon dioxide in ice is very much less than in liquid water, most of the gas separates when the water freezes. Consequently, a high gas pressure is built up inside the bottle, and this pressure may be sufficient to cause either the bottle cap to blow off or the bottle to "explode." In either case the end result is unsatisfactory.

It is not possible to arrive at any reliable generalizations with respect to the influence of temperature upon the solubility of liquids in liquids. In some cases the solubility increases with increase in temperature, in some it decreases, and others are little if at all affected.

With but relatively few exceptions, the solubility of solids in liquids increases with increase in the temperature. In some instances this increase is very great. At 25°C. , for example, the solubility of potassium nitrate in water amounts to (approximately) 31 g. KNO_3 per 100 g. H_2O . At 50° , the solubility of this same salt is (approximately) 83 g. KNO_3 per 100 g. H_2O . Other solutes such as ordinary salt show very little dependence of solubility upon temperature. Suppose, for example, that we have a saturated solution containing 83 g. KNO_3 in 100 g. of H_2O and allow this solution to cool to 25° . One would expect that solid KNO_3 crystals would separate in a quantity equal to the difference between the solubility at 50° and that at 25° (*i.e.*, $83 - 31 = 52$ g. of KNO_3 should separate from the solution). In most cases this is exactly what happens; there are, however, the inevitable exceptions. When some saturated solutions are cooled, the anticipated separation of crystals of the solute does not occur. At the lower temperature the solution consequently contains more solute than corresponds to its normal solubility. These solutions are said to be *super-saturated*, and this phenomenon is called *supersaturation*. Supersaturated solutions represent an unstable condition that may be rendered stable by agitation or by the addition of any solid particles that may act as centers for crystal growth. Thereupon the solute separates until the quantity remaining in solution corresponds to normal solubility at the prevailing temperature.

Solubility is influenced by still other factors. In some cases the solubility of one solute in a solvent is enhanced if the solvent already contains some other solute. Iodine is not very soluble in pure water, but it is much more soluble in a water solution of potassium iodide (KI). In still other cases the solubility of one solute is decreased by virtue

of the presence of another. This raises the question of the relation between solubility and the occurrence of chemical reactions. Iodine dissolves more readily in potassium iodide solution because I_2 and KI react to form a compound that is quite soluble in water. There are those who take the view that all processes of solution involve chemical changes of one kind or another. Although this may seem to be an extreme viewpoint, it finds much support in experimental fact.

Numerical values representing the solubility of solutes in solvents differ greatly depending upon the nature of the solutes and solvents. Some solutes have such low solubility values that they are classified as *insoluble* substances. Even though this is a useful adjective, it should be understood that all substances exhibit solubility, even though slight, and the use of the term insoluble merely indicates extremely low solubility. Solutions of gases in gases constitute a general exception. Since gases consist mostly of empty space and each gas behaves as though it were alone, gases may be mixed homogeneously in any desired proportions. The solubility of one gas in another is largely uninfluenced by the prevailing experimental conditions.

Finally, a clear distinction should be made between solubility and *rate of solution* (i.e., the rate at which the solute dissolves in the solvent). At 25°C ., 31 g. of finely powdered KNO_3 will dissolve in 100 g. of H_2O much more rapidly than will a single KNO_3 crystal of the same weight. The reason, of course, is that the fine powder presents more exposed surface in contact with the solvent. The end result would be the same in either case; only the rate of solution is different. In addition to the use of finely divided solute, rate of solution may be enhanced by stirring so as to bring the solvent into more uniform contact with the solute, by increasing the temperature, or both.

Methods of Designating the Quantity of Solute Present in a Solution. In strictly scientific work and in many of its practical applications, there is often need to express clearly and definitely the quantity of solute present in a given quantity of solvent or solution. That is, one needs to express the *concentration* of solutions. This may be done in a number of different ways, some of which are not very definite. Chemists speak of *concentrated* solutions, *dilute* solutions, very dilute solutions, etc. To state that a solution is concentrated conveys only the idea that the solution contains a considerable quantity of solute, perhaps a quantity approaching that corresponding to saturation.

The term "dilute" is equally indefinite and merely suggests the presence of relatively smaller quantities of solute. Although useful, these terms—like the even more indefinite terms "strong solution" and "weak solution"—are inadequate for the precise specification required.

Any solution of known concentration is called a *standard solution*, and this designation places no restriction upon the manner in which one chooses to express concentration. It is common practice to express the concentration of solutions on the basis of weight of solute per unit

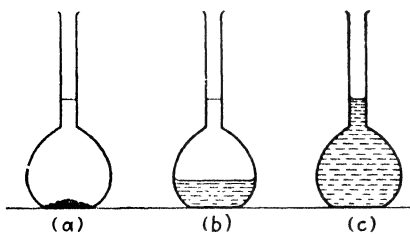


Figure 67. Preparation of a 1 *M* solution. (a) Place the required weight of solute in the flask; (b) dissolve the solute in water; (c) add enough water to bring the total volume up to the mark denoting one liter.

weight of solvent or weight of solute per unit volume of solvent. We may specify, for example, that a salt solution contains 1.65 g. of NaCl per 100 g. of H_2O , 8.5 g. per 100 ml., etc. A procedure that is much more convenient for many purposes is to express concentration in terms of the number of gram-molecular weights of solute present in some specified quantity of *solution* (rather than quantity of *solvent*). A solution containing one gram-molecular weight of solute dissolved in enough solvent to make one liter of solution is called a *molar solution* (abbreviated *M*). In the laboratory, molar solutions are prepared by placing the required weight of solute in a flask, dissolving the solute in some of the solvent, then adding enough solvent to bring the total volume up to a mark on the neck of the flask, predetermined to denote a total volume of one liter (Fig. 67). If a two molar solution (2 *M*) is required, one uses two gram-molecular weights of solute in enough solvent to make a total volume of one liter of solution; for a tenth molar solution (0.1 *M*) one uses one-tenth of a gram-molecular weight, etc. In the course of laboratory work, it is very helpful to know the concentrations of solutions in terms of molarities, to know, for example, that 100 ml. of a solution contains some definite fraction or multiple of a gram-molecular weight of solute and the corresponding number of molecules.

Molar solutions, of course, represent only one type of standard solution. Another type will be introduced in Chapter 15.

Properties of Solutions. Each of the two components of a solution—the solute and the solvent—has its own characteristic properties. When the two are together in the form of a solution, they do not retain these same properties in full measure. There are many things that occur upon formation of solutions that are poorly or incompletely understood. The addition of a solute results sometimes in an increase in volume, sometimes in a decrease, and sometimes in essentially no change. There are still other features of the interaction of solute and solvent that will have to be studied much more extensively before they are thoroughly understood.

Despite the manifold deviations in behavior that characterize the chemistry of solutions, they exhibit some surprising regularities in physical properties. It will be recalled from Chapter 9 that each pure liquid has a definite vapor pressure, boiling point, freezing point, etc. The problem to be explored now is concerned with the manner in which these properties are changed upon the addition of a solute, *i.e.*, when the pure liquids are used as solvents. For purposes of illustration, let us assume that we use four 1000-g. portions of pure water as solvent and prepare four solutions using one gram-molecular weight of each of the four solutes listed below.

Urea, CON_2H_4 (mol. wt. = 60)

Glycerine, $\text{C}_3\text{H}_8\text{O}_3$ (mol. wt. = 92)

Glucose, $\text{C}_6\text{H}_{12}\text{O}_6$ (mol. wt. = 180)

Sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ (mol. wt. = 342)

Thus, in one 1000-g. portion of water, 60 g. of urea is dissolved; in another, 92 g. of glycerine; etc. In each solution the weight of solvent is the same but the weight of solute is different. If the temperature of these four solutions is lowered to 0°C . (the freezing point of water), the water does not freeze. It is necessary to lower the temperature to -1.86°C . before crystals of ice form. The striking part of this result is that freezing occurs in all four of the solutions at this same temperature even though the weights of solute are very different. What, then, do these four solutions have in common that leads to this remarkable uniformity of behavior? To answer this question one need note only that each solution contains one gram-molecular weight of solute and hence *the same number of solute molecules* (6.02×10^{23} molecules). If

each of the solutions had contained only one-half of a gram-molecular weight of solute, the lowering of the freezing point would have been just one-half as great; freezing would have occurred at 0.93° below zero rather than at 1.86° below zero. From these and many similar experiments it is concluded that a solute lowers the freezing point of a solvent to an extent that is dependent only upon the number of solute particles present in the solution. These particles may be atoms, covalent molecules, or ions; the four solutes chosen for the preceding illustration were selected because they do not ionize in water solutions.

If the freezing-point experiment should be repeated using solutes such as sodium chloride and sulfuric acid (both of which are electrolytes), the freezing point of the water would be lowered but the extent of the lowering would be greater than the interval from 0° to -1.86° . This is to be expected on the basis of the knowledge that these solutes exist in water solution in the form of ions and their solutions consequently contain more particles per gram-molecular weight of solute.

The magnitude of the freezing-point lowering is different for different solvents and characteristic of each. Had some solvent other than water been used as an illustration, the extent to which the freezing point was lowered might have been 3° , or 5° , or some other equally definite value. Although the thought need not be pursued further, it seems worth while to point out that this and other regularities in the physical properties of solutions provide a basis for the experimental determination of molecular weights and for the measurement of the extent to which electrolytes are ionized in solution.

It is an inescapable experimental fact that the freezing point is lowered, but why this should be true may not be immediately apparent. One must return to the idea that the lowering of the temperature leads to a decrease in the kinetic energy of the molecules in the solution to an extent such that the attractive forces between molecules of the solvent can arrange them into the definite geometric pattern of the crystal. If solute molecules are present, they serve to separate the solvent molecules so that the attractive forces have to operate through greater distances. In a water solution at 0° there are enough solute molecules in between the solvent molecules so that the attractive forces are not sufficiently strong to permit crystal formation. It is necessary to lower the temperature—to decrease the kinetic energy—still more; hence the lowering of the freezing point.

One may now inquire whether all of this is merely something that keeps chemists amused and occupied or whether it is of some practical value. The familiar use of ice-salt mixtures to achieve low temperatures in the production of homemade ice cream is a direct application of knowledge gained through the study of the manner in which solutes affect the physical properties of solvents. An application bearing directly upon the lowering of the freezing point is found in the use of antifreeze mixtures in the cooling systems of automobiles. Among the substances used to lower the freezing point of water, those most commonly employed are

CH_3OH	$\text{C}_2\text{H}_5\text{OH}$	$\text{C}_2\text{H}_4(\text{OH})_2$
Methyl alcohol (Wood alcohol)	Ethyl alcohol (Grain alcohol)	Ethylene glycol (Prestone)
B.p., 64.5°	B.p., 78.5°	B.p., 197.0°
Mol. wt., 32	Mol. wt., 46	Mol. wt., 62

These substances are sold widely under various trade names. Although it is not intended to provide free advertising for any particular type of antifreeze liquid, there are certain facts concerning these substances that are noteworthy. Both methyl alcohol and ethyl alcohol suffer the disadvantage that they have boiling points lower than that of water and are thus more readily lost by evaporation. If, on the other hand, one compares the three on a weight basis, methyl alcohol (and, to a lesser extent, ethyl alcohol) possesses a distinct advantage. Comparison of the molecular weights of methyl alcohol and ethylene glycol shows that, for any given weight of antifreeze liquid selected, there will be present nearly twice as many molecules of methyl alcohol as there are molecules of ethylene glycol. Hence, on an equal-weight basis, methyl alcohol is nearly twice as effective in lowering the freezing point of water. The distinct advantage possessed by ethylene glycol is its boiling point, which is much higher than that of water; consequently, ethylene glycol is not lost by evaporation at any appreciable rate.

Attention is next directed to the influence of solutes upon the vapor pressures and boiling points of pure liquid solvents. Vapor pressure has been likened to an escaping tendency manifested when molecules from the surface layer of a liquid pass into the gaseous state. If solute molecules are present, there will be fewer solvent molecules in the surface layer (Fig. 68) and hence less opportunity for their escape.

Consequently, it is seen that the presence of solute molecules *decreases the vapor pressure* of the solvent, and to an extent that depends upon the number of solute particles present. If the four solutions containing one gram-molecular weight of urea, glycerine, glucose, and sucrose in 1000 g. of water are heated to $100^{\circ}\text{C}.$, they will not boil because the vapor pressure has been lowered enough so that it is less (at 100°) than the opposing atmospheric pressure. In order to cause boiling, it is required to increase the temperature (and, at the same time, the

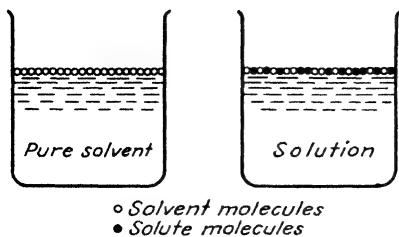


Figure 68. Solvent molecules may escape from any point on the surface of the pure solvent. Escape of solvent molecules from the surface of the solution is restricted to those areas not occupied by solute molecules.

vapor pressure) in all four cases to 100.515° . At this temperature the vapor pressure of each solution just exceeds the opposing atmospheric pressure. Again the behavior is quite regular unless solutions of electrolytes such as sodium chloride and sulfuric acid are employed. In these latter cases the vapor pressure of the liquid solvent is lowered, and its boiling point is correspondingly elevated, but to an extent greater than 0.515 .

In the operation of automobiles in desert areas advantage is taken of this increase in the boiling point of water. Addition of ethylene glycol raises the boiling point of the water used in the motor cooling system and thus lessens the loss resulting from evaporation. Still another application of the lowering of the vapor pressure of water involves the problem of dust abatement on unpaved highways. Numerous common solid substances including calcium chloride, CaCl_2 , are so soluble in water that they absorb water from the atmosphere. The surfaces of the solid particles become coated with a film of solution of calcium chloride in water. The vapor pressure of this film of solution is less than the vapor pressure of water in the atmosphere, and hence the absorption of water continues until the two vapor pressures are equal (*i.e.*, until equilibrium is established). Solids that behave in this manner are said to be *deliquescent*, and the phenomenon is called *deliquescence*. A thin layer of a deliquescent solid such as calcium chloride spread upon the surface of a dusty highway soon absorbs enough water from the atmosphere to wet the road surface and thus abate the dust. In

general, the use of so-called “moistening agents” in tobacco, leather products, textiles, and the like, involves glycerine or other very soluble substances that can absorb water from the surrounding atmosphere.

Osmosis. Another regularity observed in the properties of solutions of non-electrolytes is the phenomenon of osmosis. It has been known for a long time that certain vegetable and animal membranes such as bladder, gut, eggshell lining, and similar tissues are selectively permeable by different kinds of molecules; these are called *semi-permeable membranes*. That is, one kind of molecule can pass through the membrane while another kind either cannot or does so at a much lesser rate. If, as shown in Fig. 69, a concentrated solution of sugar in water is placed on one side of a semi-permeable membrane and pure water (or a more dilute sugar solution) is placed on the other, water molecules pass through the membrane from the pure water (or the more dilute sugar solution) into the concentrated solution. The membrane is permeable to water molecules but not to sugar molecules. This kind of selective transfer of molecules into a region where their concentration is less is called osmosis. Osmotic transfer may be prevented by the application of pressure, and that required in any given case is called the *osmotic pressure* of the particular solution.

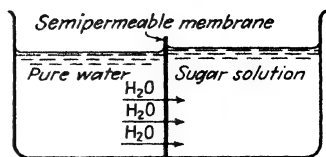


Figure 69. The osmotic transfer of solvent molecules through a semi-permeable membrane.

The phenomenon of osmosis is of far-reaching importance not only in chemistry but perhaps even more so in biology, medicine, and related areas. Animal and plant nutrition depend in considerable measure upon this type of transfer. Osmosis is responsible in part for the germination of seeds and for the rise of sap into the branches and leaves of trees. The extraction of sugar from sugar beets involves osmosis. The preservative action of sugar solution is believed to depend upon this type of selective process whereby water is transferred from bacteria into the sugar solution with resultant destruction of the bacteria.

If two solutions having the same osmotic pressure are placed on opposite sides of a semi-permeable membrane, they exist in equilibrium and there is continual but no net transfer of one kind of molecule in either direction. Such solutions are said to be *isotonic*. When there is need to inject solutions into the blood stream for medicinal, nutritional,

or replacement purposes, it is essential that the solution injected be isotonic with the blood. Otherwise an excessive transfer of water either to or from the body tissues will occur, possibly with fatal results.

EXERCISES

1. *New terms:* insoluble substance, solution, semi-permeable membrane, saturated solution, solute, osmotic pressure, supersaturated solution, molar solution, solvent, solubility, deliquescence, standard solution, osmosis, isotonic solutions.
2. Why do ionic solutes exert greater effects upon the properties of pure liquids than do covalent solutes?
3. In what ways may the rate at which a solid dissolves in a liquid be increased?
4. List all of the possible types of solutions, and indicate those which are the most common.
5. Cite some familiar occurrences that involve osmosis.
6. How is each of the following properties of pure liquids changed by the presence of a covalent solute: (a) boiling point; (b) freezing point; (c) vapor pressure?
7. How is the solubility of most solids in liquids influenced by changes in temperature?
8. How is the solubility of a gas in a liquid changed by (a) an increase in pressure; (b) a decrease in temperature?
9. Under what conditions would the use of calcium chloride for dust abatement prove wholly ineffective?
10. What two physical properties should be possessed by an ideal anti-freeze liquid for use in automobiles? Suggest one chemical property that is of outstanding importance.
11. Why would methyl alcohol or ethyl alcohol be unsuitable for use in automobile radiators during operation on the desert during very hot periods?
12. How many molecules of glycerine are present in one liter of 1.5 *M* solution of glycerine in water?
13. If one-tenth of a gram-molecular weight of alcohol is dissolved in 1000 g. of water, at what temperature would the water freeze?

14. What weight of glucose would be required to prepare each of the following solutions: (a) one liter of 2 *M* glucose solution; (b) 100 ml. of 1 *M* glucose solution; (c) 700 ml. of 0.6 *M* glucose solution?
15. A certain solution is known to contain urea, and its concentration is known to be 0.1 *M*. What weight of urea is contained in 1 ml. of this solution?

COLLATERAL READING

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Colloids

THE UTILITY of the classification of matter in terms of the three physical states has been evidenced by the manner in which solids, liquids, and gases may be studied in relation to their characteristic properties and their interrelationships. But matter may exhibit properties that are not typical of solids, liquids, or gases. When matter in any of the three physical states exists in the so-called colloidal condition, it exhibits characteristics so distinctive as to warrant a separate classification.

The chemistry of matter in the colloidal condition is essentially the chemistry of small particles and many of them. Because these may be solid, liquid, or gaseous, it is important to recognize that the colloidal condition does not represent a fourth state of matter. Rather it should be understood that the use of the term colloid implies the existence of matter in particles that are larger than atoms and ions, larger than most molecules, and yet very much smaller than individual particles which are separately visible to the unaided eye.

The General Nature of Matter in the Colloidal Condition. Perhaps the simplest approach to an appreciation of the nature of colloids is the use of a specific illustration. If a sample of ordinary sand is suspended in water by vigorous stirring, the sand quickly settles to the bottom of the container so soon as the stirring is discontinued. One may observe at the same time that the larger particles settle more rapidly under the influence of gravity than do the smaller particles. If the sand is ground to a fine powder and again stirred in water, the particles will still settle out, but much more slowly than before. A continuation of the process of grinding the solid particles to smaller and still smaller dimensions results ultimately in the production of particles so small that, when suspended in water, they will not settle out but will remain suspended uniformly throughout the body of the water. The resultant stable sus-

pension comprises one type of colloid, and the procedure just outlined illustrates one method for the production of colloids. The penitentiary inmate who works upon the rock pile, "making little ones out of big ones," carries out the preliminary stages of colloid formation.

The subject of immediate concern is the question as to how small the solid sand particles must be before they will remain in suspension in water. Actually it is not necessary that the particles be of any one specific size; it is necessary only that the diameters of these particles fall within a certain ill-defined range. Convenient designation of this range requires a unit for the measurement of length much smaller than any unit thus far introduced. It should be recalled from Chapter 8 that there are 2.54 centimeters to the inch and that each centimeter is further subdivided into ten millimeters. The distance between the tips of the two arrows, $\longrightarrow \longleftarrow$, is exactly one millimeter. If this already small distance is divided into one million equal parts, each part is one *millimicron* (abbreviated $m\mu$). In other words, one millimicron is one one-millionth of a millimeter.

We now have at hand a unit suitable for the expression of very small lengths, but we should not use it. Like others, chemists get into bad habits, and one of them is the practice of designating the limiting diameters of colloidal particles. It is no more realistically possible to do so than to answer the question: How small is a small boy? Much like small boys, colloidal particles are adjudged best in terms of their actions and behaviors and not in terms of any exacting specification of size, weight, or the like. Purely as a sop to tradition, we shall say that colloidal particles are ones having diameters within the range of 1 to 100 $m\mu$, but this statement should not be interpreted too literally.

The preceding example of a colloid consisting of a solid suspended in a liquid (a suspension) is only one of several types that might have been selected as an introductory illustration. In this particular case, the suspended solid is called the *dispersed phase*, and the liquid is called the *dispersion medium*. Either the dispersed phase or the dispersion medium may be solid, liquid, or gaseous, except that both may not be gases. One may be tempted at this juncture to draw an analogy between the terms dispersed phase—dispersion medium—colloid and the terms solute—solvent—solution. Any such apparent analogy is purely fortuitous; in colloids, the dispersed phase is not *dissolved* in the dispersion medium. The colloidal particles are *sus-*

pended, and discrete surface boundaries separate the particles of the dispersed phase and the medium in which they exist.

Properties of Colloids. Once it is agreed that the existence of matter in the colloidal condition is intimately concerned with the question

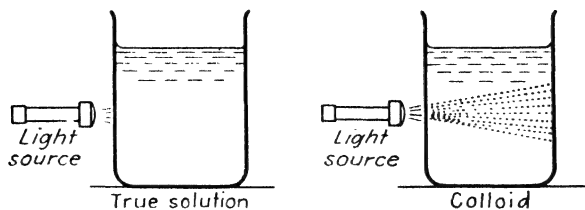


Figure 70. Tyndall effect.

of particle size, it becomes necessary to explain why and how this mode of existence should be characterized by distinctive properties. One must be able to explain, for example, why colloidal particles do not settle under the influence of gravity, why particles that have grown to colloidal size do not continue to grow, and provide answers to a multitude of similar inquiries.

A property of colloidal particles which is easy to demonstrate is that of their motion. Each particle possesses a kinetic energy which tends to

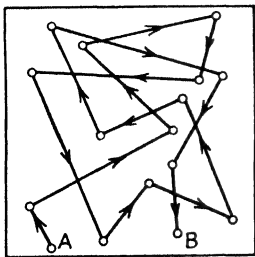


Figure 71. Brownian movement of colloidal particles.

keep it in motion, but because the individual particle consists of an aggregate of many molecules this motion is slight. On the other hand, each particle is continually bombarded by the moving molecules of the dispersion medium, and this is a major factor in the observable movement of colloid particles through the dispersion medium. If a colloidal dispersion is illuminated by a strong beam of light, the path of the light beam is readily discernible to the unaided eye because of the reflection of

light from the surfaces of the suspended particles. This is known as the *Tyndall effect* and is illustrated by Fig. 70. If one views the Tyndall cone with a high-power microscope placed at right angles to the beam of light (this arrangement is referred to as an *ultra-microscope*), the unorderly motion of the particles (Fig. 71) is readily observed. This kind of observation was first made in 1827

by the Scotch botanist Robert Brown and is known as the *Brownian movement*. Thus it is possible to apply the kinetic theory to colloidal particles even though they consist of clusters of many molecules rather than individual molecules. It is also noteworthy that the Tyndall effect provides convincing evidence of the distinction between colloids and true solutions.

By equally simple experiments it is possible to show that many colloidal particles bear electrical charges. Since the particles themselves usually consist of neutral atoms or molecules, it follows that the charge must be acquired from the surrounding medium. It turns out that the electrical properties of colloids arise because the particles have the ability to attract ions present in the dispersion medium and hold these ions on the surfaces of the colloid particles; *i.e.*, the particle, *adsorb* ions. Furthermore, it is found that colloids are highly selective in the adsorption of ions; one kind of colloid particle will adsorb only positive ions, and another will adsorb only negative ions. Since all of a given kind of colloid particles adsorb ions of the same charge signs these particles repel each other and this is another factor that tends to keep the particles in motion and to prevent their clustering together to form units larger than those that correspond to the colloidal condition.

Another contributing factor to the stability of some colloids is the presence of a protective coating consisting of a film of some gummy material such as gelatin. If the surfaces of the individual particles are so coated, it is less easily possible for them to come into direct contact and coalesce into larger particles.

In summary, it may be stated that colloids are stable because of (1) their motion, (2) their electrical charges, and/or (3) the presence of protective films.

Methods for the Formation of Colloids. In a broad sense, all methods for the preparation of colloids are classified as either *dispersion* or *condensation* processes. In the use of dispersion methods one starts with large particles and breaks them down into smaller and smaller units, finally to colloidal size. Mechanical grinding machines known as *colloid mills* are commonly employed for this purpose. In addition, some solids are disintegrated or dispersed into the colloidal condition by chemical action. Thus, when glue or gelatin is added to water, the solid is not dissolved by the water but rather is *peptized*. This behavior

is called peptization, and the chemical substance responsible is referred to as a peptizing agent. Peptization may be accomplished by numerous specific chemicals other than water, including ions.

For the most part condensation methods involve chemical reactions, many of which are relatively slow chemical changes. We may, for example, bring together two substances that can react to form an insoluble substance (a precipitate) that would be expected to separate as a solid and settle to the bottom of the container. Instead, the mole-

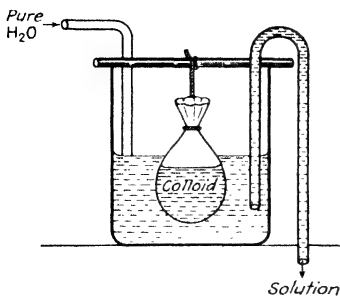
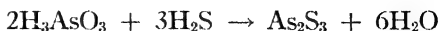


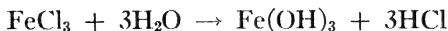
Figure 72. Purification of a colloid by the process of dialysis.

cules may coagulate to form particles of colloidal dimensions and remain in this condition rather than separate as a precipitate. Thus, the addition of hydrogen sulfide to arsenious acid produces a yellow colloidal suspension of arsenious sulfide.



The resulting arsenious sulfide particles provide a typical example of a colloid that adsorbs negative ions.

In a similar manner one may easily prepare colloidal ferric hydroxide by the reaction between ferric chloride and water.



This reddish-brown colloid contains suspended particles that adsorb positive ions. This particular type of reaction in which a cleavage is accomplished by reaction with water is called *hydrolysis*, and the substance that so reacts with water is said to be *hydrolyzed*.

These illustrations of colloid formation show how simply matter may be put into the colloidal condition. Forming colloids is usually easy; keeping them in the colloidal condition is often quite a different problem. When formed by the hydrolysis of ferric chloride, ferric hydroxide is a reasonably stable colloid but it may be rendered still more so if it is purified by the removal of the by-product HCl. This purification is accomplished by the process of *dialysis*, which involves placing the colloid within a membrane such as collodion, parchment paper, or artificial sausage skin and immersing it in pure water (Fig. 72). The membrane wall is selectively permeable to the H^+ and

Cl^- ions, and they diffuse out into the pure water, leaving behind the suspension of ferric hydroxide in water. The process may be made more efficient by maintaining a flow of fresh water around the membrane outer wall so that the impurities are removed as quickly as they move out into the water.

The Coagulation of Colloids. Partly for the reason that colloids often form when they are not wanted, it is just as important to know how to destroy colloids as it is to know how to produce and purify them. This provides another excellent example of the scientific approach to the solution of a very practical problem. Before chemists arrived at even a reasonable understanding of the factors responsible for the stability of colloids, efforts to destroy them had to be restricted to the unsatisfactory trial-and-error approach. As new information relative to the true nature of colloids was slowly accumulated, it became more and more apparent that the properties of colloids are primarily dependent upon their large exposed surfaces. Once chemists came to understand the role of adsorption upon these surfaces, the effect of adsorbed ions, protective films, etc., it became relatively easy to devise means to counteract the factors that render colloids stable and thus provide for their coagulation (precipitation).

Some colloids may be coagulated merely by boiling them. The attendant elevation of the temperature increases the kinetic energy of the colloid particles, they move more rapidly and collide more frequently and with greater force, and thus coagulation into large aggregates becomes more readily possible. These large aggregates are of greater than colloidal size; consequently they separate as a precipitate and settle out.

Another useful method takes advantage of the neutralization of the electrical charges to which many colloids owe their stability. When an electrolyte is added, the charges of the adsorbed ions are neutralized, the colloidal particles no longer repel each other, and so they may collide and stick together. Large aggregates form, and these separate as a precipitate. The same effect may be produced through a *mutual precipitation* action when a positive colloid and a negative colloid are mixed. Addition of negative arsenious sulfide to positive ferric hydroxide results in the precipitation of both.

Emulsions. Thus far, the discussion of colloids has been restricted to suspensions. There are many common materials such as milk and

mayonnaise that consist of colloids of the type called *emulsions*. The nature of emulsions can be illustrated better in terms of a simpler example. If kerosene, gasoline, salad oil, or other liquid that is insoluble in water is shaken vigorously with water, the oil is broken up into small drops that become distributed throughout the body of the water. With some pairs of liquids the oil drops are reduced to colloidal size, and they (the dispersed phase) remain suspended in the other

liquid (the dispersion medium) and constitute a stable emulsion that has a turbid or milky appearance.

More typically however, surface-tension forces cause the dispersed drops to coalesce and form larger drops so that the liquid oil and the water will expose the smallest possible surface areas. Ultimately the oil and water separate into two distinct liquid layers. In order to emulsify two liquids that behave in this manner, one must add a so-called *emulsifying agent*. Figure 73 shows one way in which such an agent stabilizes an emulsion. Oil-

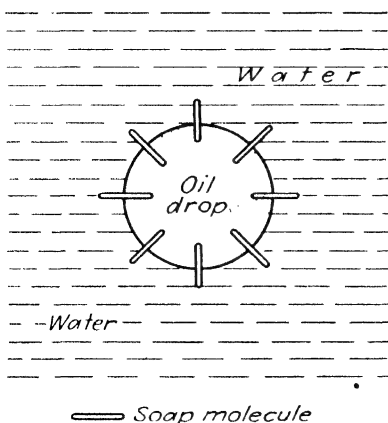


Figure 73. An oil-water emulsion stabilized by a soap.

water emulsions are often stabilized by the addition of soap because the molecules which comprise ordinary soaps (Chapter 27) are of a character such that one end of the molecule dissolves preferentially in the oil droplet while the other end dissolves in the water. In this manner the soap molecules orient themselves with respect to the dispersed phase and the dispersion medium and prevent the former from coalescing. Depending upon the nature of the emulsifying agent employed, one may produce an emulsion of oil in water or an emulsion of water in oil. Some liquids form emulsions very readily because one or more of the liquids contain as impurities substances that can act as emulsifying agents.

Devices called *homogenizers* are used in the production of emulsions and serve essentially the same purpose as colloid mills. Liquids are introduced at pressures as high as 1500 to 2000 pounds per square inch and forced outward through very fine openings (Fig. 74). This

breaks the liquid into tiny drops that remain emulsified. Mayonnaise salad dressing is produced in this manner by using a salad oil such as olive or cottonseed oil and vinegar together with egg yolk, which serves as the emulsifying agent. Homogenizers are used to disperse the cream in whole milk, and the resulting emulsion ("homogenized milk") has a uniform consistency. Many other food products are prepared similarly.

Jellies and Gels. Some colloidal particles show a remarkable ability to adsorb on their surfaces the molecules of the dispersion medium. It is possible for a large number of these particles more or less uniformly distributed throughout the body of the dispersion medium to adsorb substantially all of the molecules of the latter. Thereupon, the colloid sets to a semi-rigid mass that is described by the familiar term *jelly*. Among the more common applications of this type of behavior is the production of fruit jellies and gelatin desserts. In the formation of fruit jelly, sugar is added to strained fruit juices, which contain

the natural fruit flavors, certain acids, sugars, and substances called *pectins*. These pectins supply the particles that adsorb water, and failure to "jell" is usually the result of an insufficient supply of pectins. These failures are easily avoided by the addition of commercial pectic substances such as the product sold under the trade name Certo. A very old alternative is the housewife's practice of adding apples or apple rinds to other fruit juices in order to promote jelly formation. The reason why this practice was successful lies in the fact that apples have a high pectin content, whereas many fruits contain insufficient pectin for jelly formation. The production of jellies is another example of a procedure long employed in the home as nothing more than a hit-or-miss art but now used on a more dependable basis because of a better understanding of the nature of the changes that occur.

By careful removal of the dispersion medium from a jelly, there is produced a solid, amorphous, and extremely porous mass which is called a *gel*. Sometimes one may change a jelly to a gel merely by the

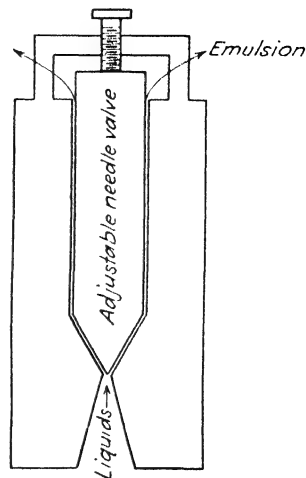


Figure 74. Principle of an homogenizer.

application of heat under controlled conditions; other cases respond better to the removal of the dispersion medium by appropriate chemical treatment. In any event the resulting gel has a porous sponge-like structure which presents a tremendous exposed surface. One of the most familiar uses for gels is their employment in gas masks as adsorbents for toxic gases. Gels are used also to adsorb malodorous gases, as selective adsorbents for a wide variety of ions and molecules in separation processes, and to remove some of the water from air in its passage through air-conditioning units. Because of their greatly extended surfaces, gels are useful as "carriers" for catalysts; *i.e.*, the catalysts are distributed over these large gel surfaces in order to provide better contact with the reactants subject to the catalytic action.

Some Products and Processes Involving Colloids. The examples that have been cited in the preceding pages at least suggest that colloidal materials and the behaviors which they exhibit play an important role in the preparation of foods. These applications of colloid chemistry in the home are so many and so varied that the art of cooking has been called "the colloidal art." Milk and cream, salad dressings, gelatin desserts, cornstarch puddings, marshmallows, jellies, etc., are only a few examples, and this list could be extended almost indefinitely. Nor does interest in colloid science cease upon preparation of foods; colloidal materials are intimately concerned with many of the vital processes sustained by these foods. The protoplasm which is the basis of all animal life is of an essentially colloidal nature. Plant and animal tissues are of colloidal character, and many of their functions depend upon the existence of matter in the colloidal condition but are as yet only imperfectly understood. From these facts alone it is clear that a knowledge of colloid chemistry is of special merit in the solution of many problems in botany, biology, physiology, medicine, and all of their related fields.

A current problem which remains unsolved in many highly industrialized areas is that of smoke abatement. Smoke is a colloid consisting of particles of solid carbon (the dispersed phase) dispersed in air (*i.e.*, an example of a gaseous dispersion medium). In recent years there has been a growing realization that smoke is more than a nuisance—it is a serious problem in relation to public health. The particles of tars, sand, carbon, etc., present in the air in the neighborhood of factories are known to lead to irritation of the mucous membranes of the

respiratory tract and may, indeed, contribute to the rising incidence of cancer of the lungs. Furthermore, the available sunlight is reduced considerably in a smoky or foggy atmosphere. It follows, therefore, that the efforts aimed at smoke abatement in large cities are motivated by higher purposes than just cleaner window curtains. The almost standard method for the coagulation of smoke colloids is that devised by F. G. Cottrell in 1911. This process consists in passing the smoke between electrically charged metal plates which bear charges of opposite sign. Here advantage is taken of the electrical charges borne by the colloidal particles; those of one charge are attracted to the metal plate bearing the opposite charge. The smoke is thereby eliminated, and at the same time the particles of carbon, which otherwise would have been carried out into the atmosphere, are collected and used as a fuel.

The term *aerosol* is used to denote colloids in which the atmosphere serves as the dispersion medium. Smoke is an aerosol, but we are more familiar with the use of this term in relation to the aerosol bombs used so widely during World War II to combat insects, particularly in tropical climates. In the use of these bombs, tiny drops of a solution of an insecticide such as DDT (Chapter 31) are propelled into the atmosphere upon release of a compressed gas. Upon evaporation of the solvent, colloidal particles of the insecticide remain suspended in the gaseous atmosphere.

The cleansing action of soaps illustrates one of the more common applications of emulsification. Dirt particles are often surrounded by a film of grease or oil and are not emulsified by water alone. It has already been shown, however, that soap acts as an emulsifying agent; and, in the act of cleansing, the grease-enclosed dirt particles become emulsified and are thus easily washed away. Where oil-water emulsion formation is not involved, the colloiddally dispersed soap lowers the surface tension of water, makes it a better "wetting agent," and thus makes it possible for the water more easily to dislodge dust and dirt particles that adhere to the skin, to fabrics, and to other surfaces.

Many applications entail the use of so-called *protective colloids*; egg yolk used in mayonnaise is an example already cited. Gelatin is so used to impart an even texture to ice cream; gum arabic is employed similarly in marshmallows. The common "penetrating-oil" lubricants contain colloidal graphite, and these colloids are stabilized by the addition of tannin, which serves as a protective colloid. A similar applica-

tion is found in the addition of certain gums and resins to stabilize the colloidally dispersed carbon in India ink.

The truly widespread application of colloidal materials should be evident from these few examples. However, they represent only a

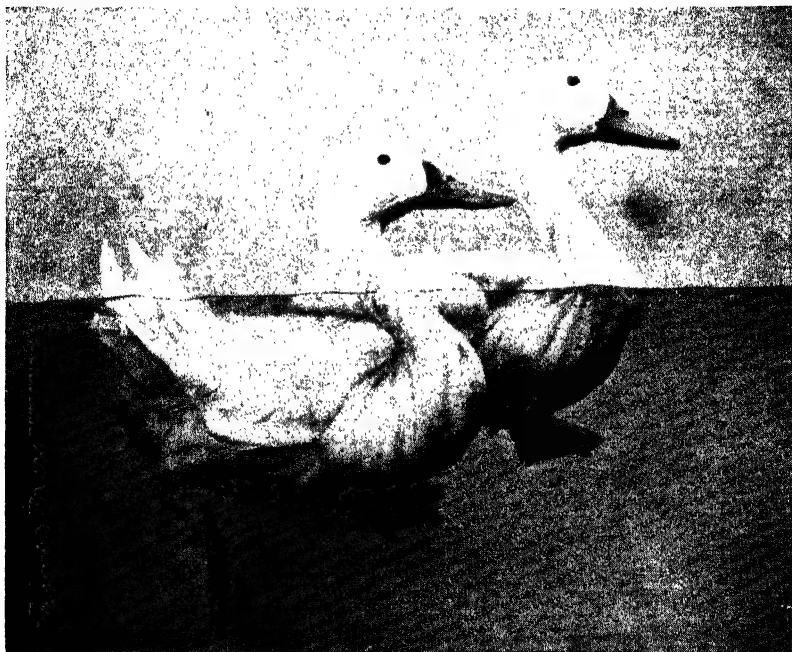


Figure 75. The duck shown in the foreground is a victim of surface chemistry. Before being placed in the water, this duck's feathers were treated with a wetting agent which lowers the surface tension of water so much that the duck is able to avoid complete submersion only by continued swimming. (Courtesy of the American Cyanamid Co.)

mere beginning. It is not a problem to think of such applications; rather it is a problem to decide what to include and what to omit. It is a simple fact that colloid chemistry provides an area of interests common to the arts, the trades, the professions, and the sciences. In addition to the specific illustrations already mentioned, others could be included that would show how colloids are important in the ceramics, dye, pulp and paper, photographic, petroleum, and other industries. Rubber, plastics, clays, and many fuels are only a few of the many familiar things that partake of the character of colloids.

EXERCISES

1. *New terms:* Tyndall effect, emulsion, coagulation, dispersion medium, millimicron, peptization, colloid, hydrolysis, gel, ultramicroscope, aerosol, dispersed phase, dialysis, emulsifying agent, jelly, Brownian movement, homogenizer, mutual precipitation, colloid mill.
2. To what factors do colloids owe their stability?
3. Give examples of colloids consisting of (a) solids dispersed in liquids; (b) solids dispersed in gases; (c) liquids dispersed in liquids.
4. How do colloids differ from true solutions?
5. Distinguish between condensation and dispersion methods for the production of colloids.
6. Explain the basis for the use of Cottrell's method for smoke abatement.
7. Explain clearly the status of colloids in relation to the three states of matter.
8. Cite three general methods for the coagulation of colloids.
9. Explain the manner in which soaps accomplish their cleansing action.
10. How does the Brownian movement provide evidence that the molecules of a liquid are in motion?
11. Distinguish between the terms *adsorb* and *absorb*.
12. If colloidal arsenious sulfide is prepared by a complete reaction between arsenious acid and hydrogen sulfide, why would it be unnecessary to purify the resulting colloid?

COLLATERAL READING

- MCPHERSON, HENDERSON, FERNELIUS, and QUILL: "Introduction to College Chemistry," Ginn & Company, Boston, 1942, Chapter 24.
- RAY: "General Chemistry," J. B. Lippincott Company, Philadelphia, 1947, Chapter 33.
- RICHARDSON and SCARLETT: "General College Chemistry," Henry Holt and Company, Inc., New York, 1947, Chapter 34.
- SCHOCH, FELSING, and WATT: "General Chemistry," McGraw-Hill Book Company, Inc., New York, 1946, Chapter XIX.

Acids, Bases, and Salts

THE STUDY of the multitude of known chemical compounds is rather considerably simplified because large segments of the total may be grouped together on the basis of similarities in the properties that they display. Chemists recognize many different *classes of compounds*, and each of these embraces hundreds of individual chemical substances. In order to merit membership in a given classification, a compound must possess certain minimum qualifications that are common to all the other substances included within the scope of the class name. The compounds belonging to a particular group may, and usually do, show considerable differences in specific properties; these, however, are differences in degree rather than in kind.

Acids, bases, and salts constitute three of the most common and useful classes of compounds. In the preceding chapters there has been no hesitation to use the word *acid* because it is a term commonly associated with "sourness." Many fruits, vinegar, "sour" milk, etc., are examples of familiar materials containing acids. Fruits, incidentally, differ greatly in their total acid content; lemons contain nearly 4 per cent acid, while bananas contain only about $\frac{1}{4}$ per cent. In addition, we are all familiar with the use of acid in automobile storage batteries (Chapter 19) and with the fact that acids corrode ("eat") metals. Bases are somewhat less prevalent in materials used from day to day but yet are represented by such common products as household ammonia, lye, slaked lime, etc. In the average vocabulary the word *salt* means only one thing, *i.e.*, ordinary table salt. The names Epsom salts, bath salts, and the like, have a broader connotation, and the term actually does embrace a very large number of compounds. The term salt is therefore a class name and one that includes soda ash, baking soda, washing soda, "bromides," "hypo," and many other common articles of commerce. Several of the compounds used previously as illustrations

(KClO_3 , KNO_3 , CaCl_2 , etc.) are salts, but it has not been necessary earlier to designate them as such.

Acids. In addition to the sour taste characteristic of water solutions of acids, they have other distinguishing properties. There are many dye molecules that are capable of existence in different forms; the dye known as *litmus* exhibits a blue or a red color depending upon the nature of its environment. If the blue form of this dye is brought into the presence of an acid, the color immediately changes from blue to red. This ability to bring about changes in the colors of dyes is a property characteristic of water solutions of acids.

The most definitive property of acids is the fact that their molecules contain hydrogen which can be replaced by metals. This was illustrated in Chapter 10, where the reaction between zinc and sulfuric acid was used to illustrate methods for the preparation of hydrogen on a laboratory scale.

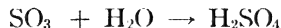
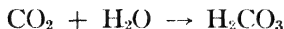
Acids may be classified conveniently in terms of the number of different kinds of elements present in the molecules. Two common binary acids are hydrochloric acid, HCl , and hydrosulfuric acid, H_2S . Attention is called to the fact that the names of these two acids begin with *hydro-* and end in *-ic*: thus there is evidence of systematization in the naming of binary acids. Most of the acids ordinarily used in the laboratory and in industry are ones the molecules of which contain the elements hydrogen and oxygen together with one other element which is largely non-metallic in character. Compounds of this type are called *ternary* acids. These acids are usually designated in terms of the identity of the element other than hydrogen and oxygen; thus we speak of acids of nitrogen, acids of sulfur, acids of phosphorus, etc. In writing the formulas of these acids the symbol of the third element is placed between those of hydrogen and oxygen.

Perhaps the commonest of all ternary acids is sulfuric acid, H_2SO_4 ; others are carbonic acid, H_2CO_3 ; nitric acid, HNO_3 ; phosphoric acid, H_3PO_4 ; and acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$. In the latter, only one of the four atoms of hydrogen is replaceable by metals, and this is emphasized by the manner in which the formula is written. With the exception of acetic acid, it is evident that all of these acids have names that include the suffix *-ic* appended to all or a part of the name of the middle element.

A fact that is always disconcerting to the beginner is that one key

element such as sulfur or nitrogen forms many acids having different formulas and, of course, different chemical and physical properties. With but very few exceptions, we shall restrict the present and all subsequent discussions to the two most common and useful acids of any particular element. The elements sulfur, nitrogen, and phosphorus, for example, form acids containing one atom of oxygen less than the acids having names ending in *-ic*; these are sulfurous acid, H_2SO_3 ; nitrous acid, HNO_2 ; and phosphorous acid, H_3PO_3 . Again there is evidence of a reasonable degree of systematic practice in nomenclature when one notes that these acids have names ending in *-ous*; this is to denote the acids of lower oxygen content.

With reference to the mode of formation of acids, commercial methods of production will be discussed in later chapters. Binary acids may be formed by several different methods, including the direct union of the two elements. Some but not all ternary acids are formed when oxides of non-metals (or metalloids) are dissolved in water.



Oxides that thus give rise to acids are called *acid anhydrides*; the literal meaning of the word anhydride is "without water."

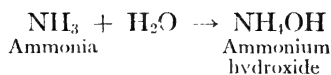
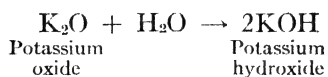
Bases. Compounds belonging to the class known as bases possess properties decidedly different from acids. The few bases that dissolve in water form solutions that have a bitter taste and feel "soapy," and most of them have a pronounced irritant effect when they come into contact with the skin. Bases are also capable of changing the colors of certain dyes; thus the color of litmus is changed from red to blue in a basic environment. In much the same way that replaceable hydrogen is the common component of all acids, so the OH group (*i.e.*, the hydroxyl ion, or hydroxyl radical) is the component common to most but not all bases.

Only a few of the bases exhibit appreciable solubility in water; these include sodium hydroxide, NaOH ("caustic soda," "lye"); potassium hydroxide, KOH ("caustic potash"); calcium hydroxide, $\text{Ca}(\text{OH})_2$ ("slaked lime"); and ammonium hydroxide, NH_4OH ("household ammonia," "aqua ammonia," etc.). Most of these substances are employed in numerous products used in the home; most of the trade

products used to clean drainpipes and other plumbing consist largely of (or at least contain) sodium hydroxide.

It is evident that the names of the bases consist of the word *hydroxide* together with the name of the element or radical in combination with the hydroxyl group. In addition to the terms base and hydroxide, these compounds (and more particularly KOH and NaOH) are often referred to by the use of the term *alkali*.

The mode of formation of calcium hydroxide by the reaction between quicklime and water has been discussed earlier. As shown by the following equations, other bases are formed similarly:



Most hydroxides are insoluble in water and cannot be produced in the manner illustrated by the preceding equations; less direct methods must be employed.

Neutralization. Before proceeding with the discussion of salts it is worth while to give attention to the nature of the chemical change that occurs when acids and bases react with each other. This type of reaction is one of the commonest methods for the formation of salts, particularly on a laboratory scale.

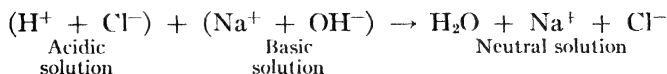
A clear understanding of the nature of acid-base reactions requires that one have clearly in mind the nature of the acidic and basic solutions and the ionic species that are responsible for the corresponding sets of characteristic properties. Let us suppose, for example, that we have at hand one liter of 1 *M* solution of hydrochloric acid. By definition, this water solution contains one gram-molecular weight of HCl (1.008 + 35.457 = 36.465 g.). In the HCl solution there are *hydrogen ions* (H⁺) and chloride ions (Cl⁻). The former are responsible for the properties of acidity; the chloride ions are wholly incidental. Suppose further that we have one liter of a 1 *M* solution of sodium hydroxide which, of course, contains one gram-molecular weight of dissolved NaOH (22.997 + 16.000 + 1.008 = 40.005 g.). This solution contains sodium ions (Na⁺) that—like the chloride ions in the acid solu-

tion—are incidental; the properties of basicity are entirely those of the hydroxyl ions (OH^-) that are present in the solution.

We have then, two solutions, and each possesses characteristic properties. If the one is added to the other, *the resulting mixture has the properties neither of an acid nor of a base* and is therefore said to be *neutral*. This is simply an experimental fact, and in order for it to be true the acidic solution and the basic solution must have reacted in a manner such that the ions responsible for acidic and basic properties were eliminated. In other words, the acid-base reaction must in reality be one between hydrogen ions and hydroxyl ions.



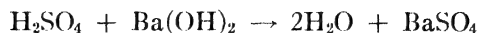
This amounts to saying that two ionic species have combined to form a covalent compound which, by virtue of its very slight ionization, furnishes only very low and identical concentrations of hydrogen and hydroxyl ions. Since neither H^+ nor OH^- predominates, the resulting solution can exhibit neither the property of acidity nor that of basicity. But what of the sodium and chloride ions? The answer to this question is very simple: they were present in the solutions before the occurrence of the acid-base reaction, they took no part in it, and they were still present as such after the reaction was complete. The over-all picture may be represented as



and the solution that is the product of the reaction consists of a water solution containing sodium ions and chloride ions. If this solution is evaporated to dryness, these ions separate in the form of solid crystals of the salt, sodium chloride.

The purpose of this rather lengthy description of a simple acid-base reaction is intended to show that the interaction of *any acid* and *any base* is essentially the reaction between hydrogen and hydroxyl ions and that the concomitant potential formation of a salt is a fortuitous circumstance. There are, of course, many cases in which the negative ion of the acid and the positive ion of the base correspond to a salt which is insoluble in water. In these instances it is not necessary to evaporate

the solution in order to recover the by-product salt in solid form; it will separate as a precipitate owing to its insolubility in water. Thus, barium sulfate (a salt) separates as a product of the reaction between sulfuric acid and barium hydroxide.



In view of the facts outlined above, it is appropriate to define neutralization as the formation of water by the reaction between the hydrogen ions supplied by an acid and the hydroxyl ions furnished by a base.

There are many common examples of neutralization. The stinging sensation caused by insect bites is attributable to the fact that the insects inject certain organic acids (Chapter 27) into the tissues. The familiar remedy of treating ant bites and bee stings with household ammonia depends upon the neutralization of the acids by the base, ammonium hydroxide. Another case that is worthy of especial emphasis involves the minor ailment known as "acid indigestion." It is a well-established fact that the normal condition of the human stomach entails the maintenance of a low concentration of hydrochloric acid and that excess acidity leads at least to discomfort and possibly to more serious consequences. Through the medium of radio, newspaper, and other forms of advertising we are exhorted to "alkalize" with all sorts of patented medicines. The purpose of the present digression is to point out the potential dangers inherent in the indiscriminate use of such products. If one thus neutralizes the excess acidity in the stomach, it is likely that the dosage of the "remedy" will be sufficient to neutralize also the normal acidity and thus render the contents of the stomach basic (alkaline). Because this is an abnormal state of affairs, additional acid production is stimulated and this may lead to a level of acidity even higher than that which existed before the alleged remedy was taken. Thus is initiated a vicious cycle which requires that one take more of the remedy. This may be good for the patent medicine business, but it may be correspondingly bad for the stomach. It must be clearly recognized that it is no more the function of the chemist to prescribe for human ailments than it is for the manufacturer of "alkalizers" to do so—even though the chemist should be the better qualified. This responsibility lies solely within the province

of the medical profession. It is not the purpose here to discourage the use of any remedy but rather to encourage any such use under the guidance of those most competent to avoid otherwise unforeseen consequences.

Standard Solutions of Acids and Bases. Probably no classes of chemical compounds are employed more commonly in the laboratory from day to day in the form of solutions of known concentration than are acids and bases. For the many uses of standard solutions of these compounds one could, of course, utilize molar solutions or fractional molar solutions. It is a matter of no little convenience, however, to be able to employ standard solutions of acids and bases containing quantities of H^+ and OH^- ions that are directly related to the fundamental chemical change that occurs when these two classes of compounds react with each other. It is convenient, for example, to have a kind of standard solution such that any given volume of acid solution would contain the quantity of H^+ required exactly to neutralize the OH^- present in the same volume of solution of a base. That is, the two solutions should be exactly equivalent on a volume-for-volume basis. This may or may not be true of molar solutions. One liter of 1 *M* HCl solution is exactly equivalent chemically to one liter of 1 *M* NaOH solution because the former contains 1.008 g. of H^+ while the latter contains 17.008 g. of OH^- . On the other hand, one liter of 1 *M* H_2SO_4 is *not* equivalent to one liter of 1 *M* NaOH solution because the molar sulfuric acid solution contains 2×1.008 g. of H^+ , and this is twice the amount required to react with the 17.008 g. of OH^- present in the molar sodium hydroxide solution.

It is evident that what we need is a kind of standard solution so defined that acid-base equivalence will be achieved. This kind of standard solution is called a *normal solution*¹ (abbreviated *N*) of an acid or a base. A normal solution of an acid is one that contains 1.008 g. of replaceable hydrogen contained in a total volume of one liter of solution. Similarly, a normal solution of a base is one that contains 17.008 g. of OH^- in a total volume of one liter of solution. Of course,

¹ Although the present discussion is restricted to normal solutions of acids and bases, it is possible to define normal solutions of salts in a no less precise manner. These should not be confused with the familiar *normal saline solution* that is used so commonly in medicine and is isotonic with human blood. Such a solution is prepared by dissolving $2\frac{1}{2}$ level teaspoonfuls of sodium chloride in a quart of water. Normal solutions of salts as used by the chemist are made up according to somewhat more precise specifications.

solutions of acids and bases can be prepared so that they will contain any desired multiple or fractional quantities of the above amounts of H^+ and OH^- . Thus, one may prepare 2 *N*, 10 *N*, 0.5 *N*, 0.1 *N*, or solutions having other specified concentrations, and the procedure for preparing them is exactly the same as that described earlier (Fig. 67).

It was pointed out that a 1 *M* solution of H_2SO_4 is not equivalent to the same volume of 1 *M* NaOH solution. A 1 *N* solution of H_2SO_4 is, however, exactly equivalent chemically to the same volume of 1 *N* NaOH solution. This must be true by definition, because the 1 *N* solution is prepared so that it contains 1.008 g. of H^+ ; this is done by dissolving one-half of a gram-molecular weight of H_2SO_4 (rather than one gram-molecular weight) in enough water to make a liter of solution.

Titration. A common laboratory procedure is that in which one measures the volume of one solution required for a reaction with another solution. This procedure is carried out by placing a known volume (or weight) of one solution in a beaker and adding to it the other solution, which is dispensed from a burette (Fig. 76). The burette bears interval markings corresponding to definite volumes (*i.e.*, it is "calibrated") so that one may read directly the volume of solution that has been delivered into the beaker.

The next problem to be faced is that of knowing when one has added from the burette just the right amount of solution for a completed reaction with that in the beaker. In other words, one must have a means of knowing when the *end-point* of the reaction in question has been reached. Chemists have exercised much ingenuity in devising both simple and elegant methods for the detection of the end-points of all sorts of chemical reactions. The present discussion will be limited

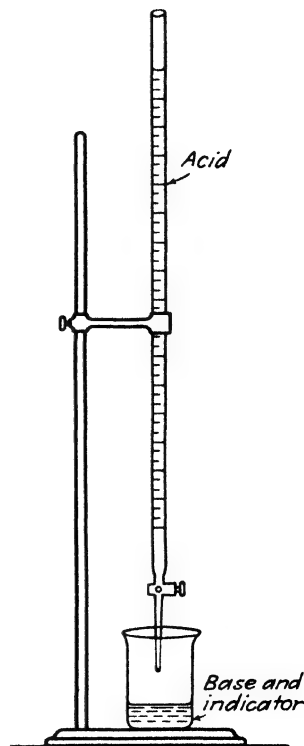


Figure 76. Titration of a base with an acid.

to the problem of detecting the end-point in acid-base reactions, and the student should be able at this point to suggest at least one method whereby this may be accomplished. If, for example, one wishes to titrate a solution of a base (contained in a beaker—Fig. 76) with an acid solution delivered from a burette, it is necessary only to add to the basic solution a dye that exhibits different colors in the presence of acid and base. Let us suppose that the dye is one which is green in basic solution and red in acidic solution. As acid is added from the burette, the solution in the beaker remains green so long as any unneutralized OH^- ions remain. Finally, upon addition of a drop of the acid solution, the last of the OH^- ions will be neutralized, and a slight excess of H^+ will prevail in the solution in the beaker. Thereupon, the dye color will change from green to red, and one knows immediately that the end-point in the acid-base reaction has been reached and that addition of acid from the burette should be discontinued. Any dye or other substance thus used to detect the end-point of a chemical reaction is called an *indicator*. After having added enough of the acid solution to reach the end-point, the volume added is read from the burette. One then has available the information needed to make numerous useful calculations relating to the quantities of acid and base involved in the reaction.

The determination of the acid content of commercial vinegar serves as a useful example of a practical acid-base titration. To simplify the picture somewhat, it will be assumed that all of the acidity of the vinegar is due to acetic acid and that our problem is merely to determine the percentage of acetic acid in a sample of vinegar purchased at the grocery. The procedure and calculations are illustrated as follows: A 50-g. sample of the vinegar is weighed out in a beaker, and a drop of a suitable indicator solution is added. This mixture is stirred while 1 *N* sodium hydroxide solution is added from the burette until the end-point is reached; this requires 46.6 ml. of the sodium hydroxide solution. One liter of 1 *N* sodium hydroxide solution contains 40 g. of NaOH; hence 1 ml. contains $40/1000$, or 0.04, g. NaOH and 46.6 ml. contains $46.6 \times 0.04 = 1.86$ g. NaOH. This is the *weight* of NaOH that was present in the 46.6 ml. of solution added from the burette as the requirement for the neutralization of the acetic acid present in the vinegar sample taken for analysis. We now know the weight of NaOH

required to neutralize an as yet unknown weight of $\text{HC}_2\text{H}_3\text{O}_2$. From the equation for the reaction,



one may calculate the corresponding weight of $\text{HC}_2\text{H}_3\text{O}_2$, using the method outlined in Chapter 4. Thus it is found that the 50-g. sample of vinegar contains 2.79 g. of $\text{HC}_2\text{H}_3\text{O}_2$, and this corresponds to $2.79/50 \times 100 = 5.58\%$. The United States Department of Agriculture specifications require that the total acid content of a commercial vinegar may not be less than 4 per cent.

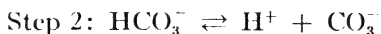
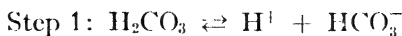
Salts. The many compounds classed as salts not only account for the major portion of the earth's crust but also constitute the prime raw materials for the inorganic-chemical and related industries. Because there are so many different types of salts and because they are used in so many familiar products purchased at the grocery, drugstore, etc., it is beyond the scope of the present chapter to consider either individual cases or broad classes of salts. Some of the more important types are discussed in Chapter 16; still others enter into the discussions included in Chapters 18, 22, and 31.

Two methods whereby salts may be formed have already been mentioned; these are the reactions between metals and acids and those between acids and bases. In addition, there are many other types of chemical changes that yield salts as either the principle products or the by-products. These methods need not be elaborated upon here since they involve detailed considerations that are likely to be useful only to those who plan on a more detailed study of chemical science. It is desirable for present purposes only to indicate that ordinarily the optimum method for the preparation of any given salt can be selected from many known possibilities based upon technical information accumulated over a very long period of time.

Finally, it should be pointed out that classifications of chemical compounds are not always absolute. Some compounds are at the same time susceptible to classification as bases and as salts (*i.e.*, they are *basic salts*). Similarly, there are compounds that partake of the character of both acids and salts, and these are called *acid salts*. Calcium bicarbonate, which was involved in the discussion of water treatment,

is a typical example; ordinary sodium bicarbonate, NaHCO_3 (or, more properly, sodium hydrogen carbonate), is a still more familiar one.

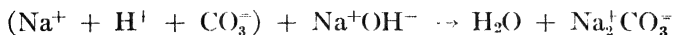
The existence of acid salts depends upon the fact that acids containing more than one replaceable hydrogen ion per molecule ionize in steps, so to speak, and hence may be neutralized by bases in a step-wise fashion. The ionization of the weak acid, H_2CO_3 , is represented by the equilibria



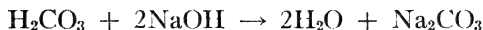
If one wishes to prepare the acid salt, NaHCO_3 , one adds only enough NaOH to provide OH^- ion sufficient to combine with the H^+ available from Step 1.



This salt, $\text{Na}^+\text{HCO}_3^-$, contains a negative ion capable of ionization (as in Step 2) to provide another H^+ , which can combine with the OH^- from another gram-molecular weight of NaOH and at the same time lead to the formation of the *normal* (non-acid) salt, Na_2CO_3 .



If the two preceding equations are now combined, the complete neutralization of the original carbonic acid is represented by a single equation.



So it is that either acid salts or normal salts are formed; the latter term refers to salts resulting from the complete replacement of the replaceable hydrogen from acids. For the reason that acid salts still contain replaceable hydrogen, they may be and in fact frequently are employed as acids.

EXERCISES

1. *New terms:* ternary compound, basic salt, normal solution of an acid, neutralization, base, indicator, normal salt, neutral solution, acid,

titration, acid anhydride, normal solution of a base, acid salt, end-point.

2. Write equations for two general methods for the preparation of salts.
3. Describe briefly the procedure for the conduct of a simple acid-base titration.
4. Justify the statement that a salt consists of the positive ion from a base, in combination with the negative ion of an acid.
5. Summarize the characteristic properties of (a) acids; (b) bases.
6. Write the equation for the fundamental reaction of neutralization.
7. Write equations showing how each of the following acids ionizes: (a) HCN , (b) H_2SO_3 , (c) H_3PO_4 .
8. Show why it must be true that one liter of 1 *N* acid will neutralize two liters of 0.5 *N* base.
9. Prove that a 1 *M* solution of H_2SO_4 is 2 *N*.
10. What is the normality of a 2 *M* solution of H_3PO_4 ?
11. What weight of HNO_3 would be required to prepare five liters of 0.01 *N* nitric acid solution?
12. What weight of KOH would be required to prepare 400 ml. of 2.5 *N* potassium hydroxide solution?

COLLATERAL READING

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MCPHERSON, HENDERSON, FERNELIUS, and QUILL: "Introduction to College Chemistry," Ginn & Company, Boston, 1942, Chapter 15.

RICHARDSON and SCARLETT: "General College Chemistry," Henry Holt and Company, Inc., New York, 1947, Chapter 23.

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Some Common Salts

THERE are so many hundreds of compounds classed as salts that it might seem difficult to select suitable examples for inclusion in any brief discussion of them. The decision is actually rather easy because it seems appropriate to restrict the present discussion to salts that are directly or indirectly involved in products or processes that have been or are likely to be encountered by the student in his day-to-day experience. With but few exceptions, this restriction will be observed in the following pages.

Classification of Salts. The manner in which salts are produced by reactions of acids with either metals or bases has been described in preceding chapters. The implicit relationship between salts and acids provides a convenient basis for the classification of salts even though they may be prepared by a variety of reactions that do not include acids among the reactants. This system of classification requires only that we consider each acid to be the "parent" of a family of salts.

Hydrochloric acid, for example, contains hydrogen (H^+) and chloride (Cl^-) ions. If the hydrogen ions are displaced by reaction with several different metals, these reactions will lead to a corresponding number of different salts. But these salts all have one feature in common: they all contain chloride ions and consequently are called *chlorides*. Accordingly, it is convenient to look upon all such salts as related to hydrochloric acid even though the salts may exhibit a wide range of physical and chemical properties. Procedures of classification that arise out of purely genetic relationships are quite common not only in chemistry but in the related sciences as well.

In relation to each acid, there is a class of salts that is named to correspond to the name of the negative ion of the parent acid. Thus, nitric acid furnishes nitrate ions (NO_3^-), and the salts that contain this ion are called *nitrates*. In an entirely analogous manner, sulfurous acid and its salts contain the sulfite ion, and the latter are known as

sulfites; salts of carbonic acid are the *carbonates*; those of phosphoric acid are *phosphates*; etc.

Sodium Chloride. For the reason that it is a typical example of the chlorides and because of its great economic importance, sodium chloride is the only representative of its class that is considered here in detail. There are many other chlorides, but none that rivals ordinary salt on almost any basis one may wish to select.

The history of salt reveals its significant role in human affairs. Salt has been known and used at least as far back as there is recorded history, and there are numerous references to this commodity in the Bible. In the time of the early Greeks and Romans, state monopolies of salt resources were maintained; salt was used as a medium of exchange and was given as pay for the services of domestics, soldiers, and other hired help (the word salary is derived from the Latin word meaning salt— hence the saying “not worth his salt”). Sodium chloride supplies have had an important bearing upon the development of industries, have determined the location of settlements during periods of colonization, and have been a determining factor in the course of wars. The development of heavy chemical industries in Europe was retarded for many years because of oppressive taxes upon salt. Following the Napoleonic Wars, England levied a tax of \$150 per ton on salt in order to replenish her badly depleted treasury. When this tax was removed in 1823, the price of salt dropped from \$160 to \$10 per ton. Some historians consider that salt supplies had a profound influence upon the outcome of the War between the States.¹ During the latter part of World War II, Germany was forced to resort to the use of many of her salt mines for bomb-proof storage and for manufacturing operations. These diversions resulted in a drastic curtailment of salt production, and this in turn led to shortages in supplies for Germany's chemical and related industries and thus contributed to the ultimate collapse of her war effort.

Whole volumes have been written on the importance of salt in the economic developments of both ancient and modern times, and it is therefore not feasible here to attempt to do more than focus attention upon salt as a strategic material in both peace and war. The close parallelism between salt production and general business activity in the United States is portrayed clearly by Fig. 77.

¹ Lonn, “Salt as a Factor in the Confederacy,” W. Neale, New York, 1933.

Commercial Production of Salt. It is fortunate for mankind that salt is so widely distributed. Vast quantities of this substance occur in many localities, and the utilization of these deposits is so often on a localized basis that it is well-nigh impossible to make anything approaching an accurate estimate of world production. The famous Stassfurt and Salzburg deposits in Central Europe are among the best known, and these salt beds contain potassium and magnesium salts in addition to sodium chloride. The waters of the seas and of lakes

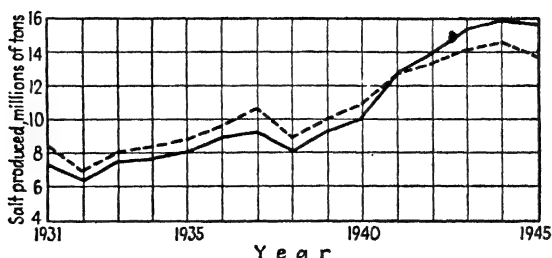


Figure 77. Salt production and general business activity. The solid line represents salt produced in the United States; the broken line is *The New York Times* Index of Business Activity. (Courtesy of the Worcester Salt Company and *The Journal of Chemical Education*.)

such as the Great Salt Lake in Utah and the Dead Sea in Palestine comprise a vast reservoir of sodium chloride. The water of Great Salt Lake, for example, contains $1\frac{1}{3}$ to 2 lb. NaCl per gallon, and the relatively high density of this salt solution is responsible for the fact that many objects which float upon it would sink in "fresh" water. Oceanic waters contain only about 3 per cent of salts including much sodium chloride (*ca.* $\frac{1}{4}$ lb. per gallon), together with lesser quantities of compounds of some thirty other elements. However, if one recalls that approximately three-fourths of the earth's surface is covered by oceanic waters, it is evident that this source alone provides a wealth of raw materials of which salt is only one. It has been estimated that the seas contain enough salt to cover the entire United States to a depth of one and one-half miles.

The annual production of salt in the United States alone amounts to about fifteen million tons. In the order of their contribution to the total, Michigan produces far more than any other state and is followed by New York, Ohio, Louisiana, Texas, Kansas, California, West Vir-

ginia, and Utah. All of the remaining states in which there is any salt production at all contribute only about 3 per cent of the total. Essentially three different methods are employed for the production of salt in the various geographical areas of this country.

A common practice in salt production utilizes energy from the sun to evaporate oceanic or other waters of high salt content. This method is suitable only in areas having limited rainfall and where high temperatures and dry winds prevail. Although this practice is prevalent in Spain, Portugal, Japan, China, and India, the so-called "solar salt industry" has reached an appreciable scale of development in the United States only in California. Water from the Pacific Ocean is pumped into large earthen vats that cover hundreds of acres, and there the water is evaporated until the salt crystallizes. In the lower San Francisco Bay area, approximately 20 tons of salt per year can be produced from vats covering an area of one acre. The California production of salt by solar evaporation amounts to nearly one-half million tons per year. Because of the other salts that are present in the waters utilized, sodium chloride produced in this manner is ordinarily less pure than that originating in underground deposits.

The bulk of the salt supplies in the United States is produced from either wells or mines. In the arid and semi-arid regions of the Southwest, salt deposits lie relatively much nearer the earth's surface than in other regions. The salt beds of Louisiana and Texas constitute the greatest reserve supplies known in this or any other country. At one location in Harris County, Tex., drillings penetrated over 5000 feet of rock salt and yet failed to reach the bottom of the deposit. Most salt deposits in this country, however, lie far below the surface; in some localities it is necessary to drill to depths as great as 2500 feet before salt beds are reached. There the sodium chloride may exist as either solid rock salt or as a natural brine. Salt production via wells (Fig. 78) involves either forcing the natural brine to the surface or the injection of water to form an artificial brine that is thereafter brought to the surface. In either case, water is forced into the well under pressure (supplemented if necessary by compressed air pressure), and the brine is forced out through a pipe and into vessels of a nature dependent upon the type of process to be employed in the recovery and purification of the salt. Some of these processes provide salt having a purity as great as 99.95 per cent.

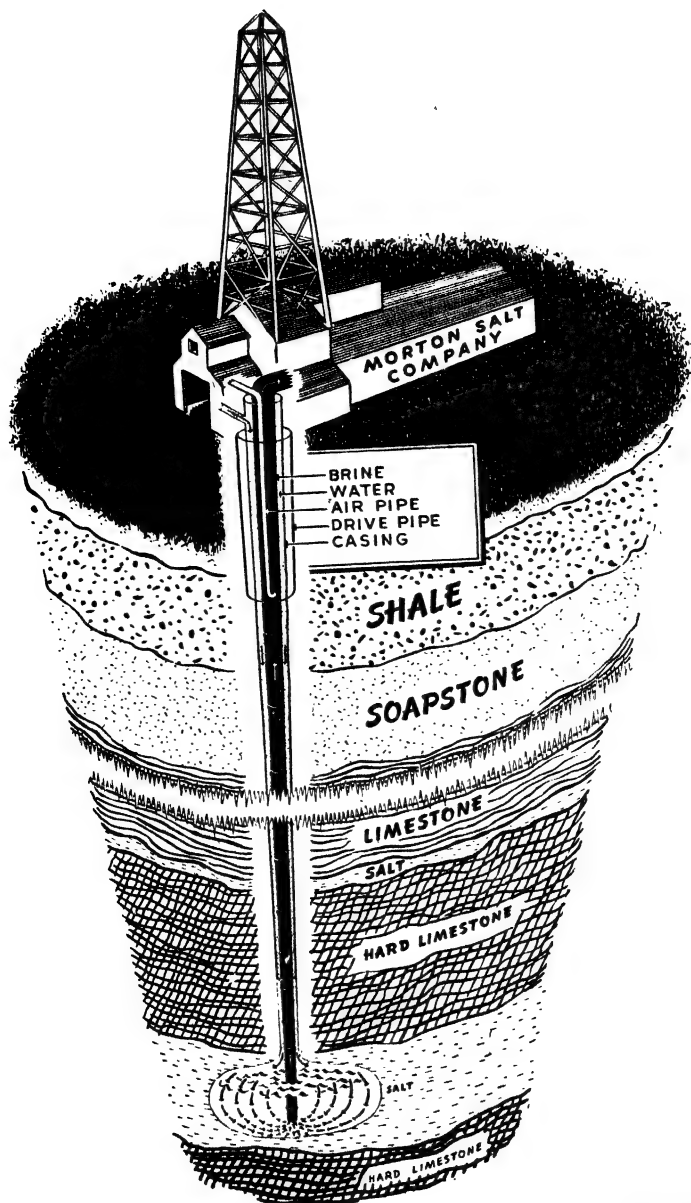


Figure 78. Diagram showing the essential features of a typical salt well. (Courtesy of The Morton Salt Co.)

The mining of salt (Fig. 79) is carried out by methods similar to those used in shaft mining for coal. Rooms that radiate from a central shaft are cut into the salt beds, which are many feet thick. The salt is dislodged by blasting, then loaded into cars, and carried to the surface. Although most of the cars are moved by electric power, mules are still used in some mines and it is not uncommon for these animals to live underground for more than ten years without ever seeing the light of

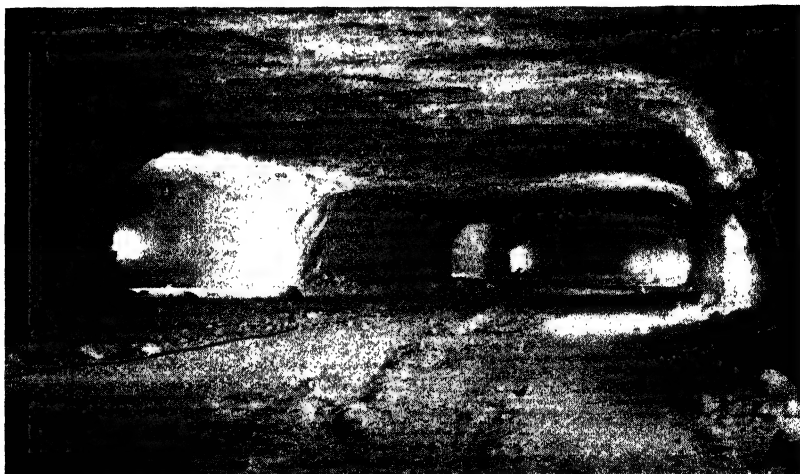


Figure 79. A view of the interior of a salt mine located at Grand Saline, Tex. The floor of this tunnel is 700 feet below the surface of the earth, and the distance from floor to ceiling is 16 feet. (Courtesy of *The Morton Salt Co.*)

day. In contrast to most mines, those which produce salt are said to entail unusually healthful working conditions.

Uses of Salt. The use of salt for the seasoning and preservation of foods is undoubtedly one of the oldest applications. Homer's "Odyssey" contains a reference to "inland peoples who eat no salt with their food," the implication being that they were too far removed from the sea, which was the chief source of supply. With reference to its use in the seasoning of food, salt has been aptly—albeit inelegantly—described as "Something that don't taste good when it ain't there." Even more important is the manner in which salt serves to prevent spoilage in many different foods, particularly meats. Some producers of table salt add 0.02 per cent NaI (sodium iodide) and sell this

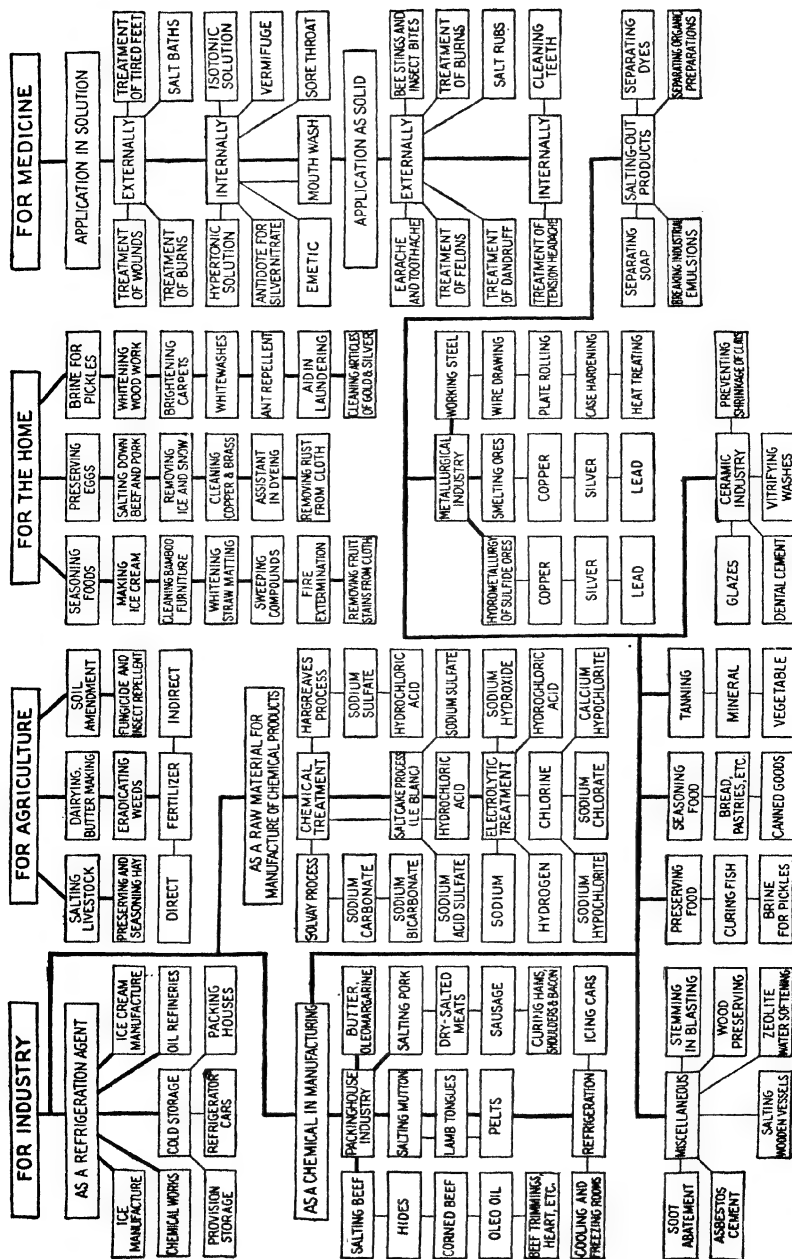
"iodized salt" on the basis of the idea that it will supplement the supply of iodine to the body and thus minimize the incidence of goiter. Profound physiological effects result from a deficiency of salt in the body; the consumption of salt tablets to combat fatigue is common practice in hot climates where there is an excessive loss of salt via perspiration. The chloride ions present as hydrochloric acid in the gastric juices of the stomach (*ca.* 0.6 per cent HCl) has its origin in sodium chloride. Both in and about the home, salt is used in many different ways, including its application as a cleanser, an antiseptic, in tooth paste, as a weed killer, etc.

The uses of salt are so many and so varied that a complete list of its applications has probably never been compiled; some of the more important ones are incorporated in Fig. 80.

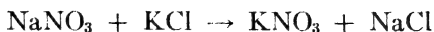
Nitrates. Of the many salts of nitric acid, only the sodium, potassium, and ammonium salts merit detailed consideration.

Sodium Nitrate. The sodium salt, NaNO_3 , is the only nitrate that exists in nature in large quantities. Since sodium nitrate is very soluble in water, it is not surprising that the naturally occurring deposits are found only in very dry regions. The chief source for many years has been the high arid coastal regions in Chile; this, of course, is the reason why sodium nitrate is known as *Chile salt-peter*. When the term *nitrate* stands alone, it denotes sodium nitrate in just the same way that the term *salt* means sodium chloride. The Chilean nitrate deposits range in depth from 5 to 15 feet, are as much as 200 miles long, and consist of a crude material called *caliche*, which contains from 50 to 60 per cent NaNO_3 . The crude solid is leached with water and filtered to remove insoluble impurities, and the NaNO_3 is recovered from the resulting solutions by evaporation. The average annual imports of Chilean nitrate to the United States in the last few years amount to approximately three-quarters of a million tons. The chief uses of this and other nitrates are concerned largely with the production of fertilizers and explosives.

Potassium Nitrate. Potassium nitrate occurs in nature in a few very dry areas in the Orient, but these deposits are not of major significance in relation to the quantities actually used in industry. Potassium nitrate is known as *salt-peter*. This is another salt that is used as a food preservative and is the one that imparts a characteristic red color to meats. The physiological effects of the salt are such as to render it useful for certain purposes in medicine. In addition, much larger quan-

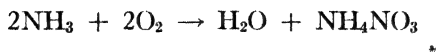


tities of potassium nitrate are employed in the manufacture of black powder, most of which is used to produce ammunition for small fire-arms, blasting powder, etc. Potassium nitrate is produced directly from nitric acid, but most of our domestic supplies are formed from sodium nitrate and potassium chloride.



This reaction is one of particular interest because all four of the salts represented in the equation are soluble in water. However, of the four, sodium chloride is the least soluble; and if one mixes hot solutions of sodium nitrate and potassium chloride and then cools the mixture, sodium chloride crystals are the first to separate. After removal of this salt, the solution still contains potassium ions and nitrate ions, and these can be recovered in the form of solid potassium nitrate by evaporation of the water from the solution. This general type of reaction is that which chemists call *metathetical reactions*, or it is referred to as the process of *metathesis*. An inspection of the preceding equation shows that the ions simply "change partners." If one inspects similarly a typical neutralization reaction or a reaction of hydrolysis, it is seen that they also are processes of metathesis. In contradistinction to oxidation-reduction reactions, those reactions which are classed as metathetical are ones in which none of the reactants either loses or gains electrons.

Ammonium Nitrate. The compound having the formula NH_4NO_3 is made available when nitric acid is neutralized by ammonium hydroxide. In commercial-production practice, the formation of ammonium nitrate results from a rather complex series of reactions starting with the interaction of gaseous ammonia and gaseous oxygen. The over-all result of these reactions may be expressed rather simply by the equation



Ammonium nitrate is an unusual compound in many respects. It is one of the most water-soluble compounds known. The solubility in water even at 0°C . is 118 g. NH_4NO_3 per 100 g. of H_2O ; at 100° ,

the solubility is 870 g. NH_4NO_3 per 100 g. of H_2O . Another unusual property is that of existing in several different crystal forms at different temperatures.

A reaction of ammonium nitrate that is of more than passing interest is its thermal decomposition to produce nitrous oxide,



which is the anesthetic known as *laughing gas* and used in dental surgery and for numerous types of minor surgical operations. (See Chapter 30.)

The use of ammonium nitrate as a fertilizer and as an explosive is discussed elsewhere in this book. It is worth while here to point out that ammonium nitrate intended for use in soil fertilization may turn out to be an explosive if carelessly or improperly handled. There have been several serious accidental detonations. In 1921, the explosion of 4500 tons of a mixture of ammonium nitrate and ammonium sulfate in Oppau, Germany, caused the loss of 450 lives. Some 700 homes were destroyed in the blast, which was felt 150 miles away and dug a crater 250 feet in diameter and 50 feet deep. In more recent times, the well-known Texas City disaster of April, 1947, provided another tragic example of the destructive force of ammonium nitrate explosions. There, more than 3000 tons of ammonium nitrate cargo exploded in the holds of the former Liberty ships, S. S. Grandcamp and S. S. High Flyer. The destruction wrought by these blasts is only inadequately portrayed by Fig. 81. More than 400 deaths, 2000 injured, and property damage amounting to over \$30,000,000 were among the results of insufficient precautions in the handling of a hazardous chemical.

Carbonates. Because the parent carbonic acid molecule contains two replaceable hydrogens, the carbonates may be either normal or acid salts. Both types are included in the following paragraphs.

The Sodium Carbonates. As shown previously, the first step in the neutralization of carbonic acid leads to the acid salt, NaHCO_3 , which is the familiar "baking soda." Although this salt occurs in limited quantities in nature, the bulk of the product available commercially is produced by the *Solvay process*. This method of manufacture was invented in 1863 by two Belgian chemists, Ernest and Alfred Solvay,

whose inventive genius was rewarded by lasting fame and (incidentally) profits well in excess of one million dollars. Largely for the reason that this process provides an excellent illustration of how the economic success of a technical project depends upon a judicious use of raw materials and by-products, the Solvay process will be considered in greater than usual detail.

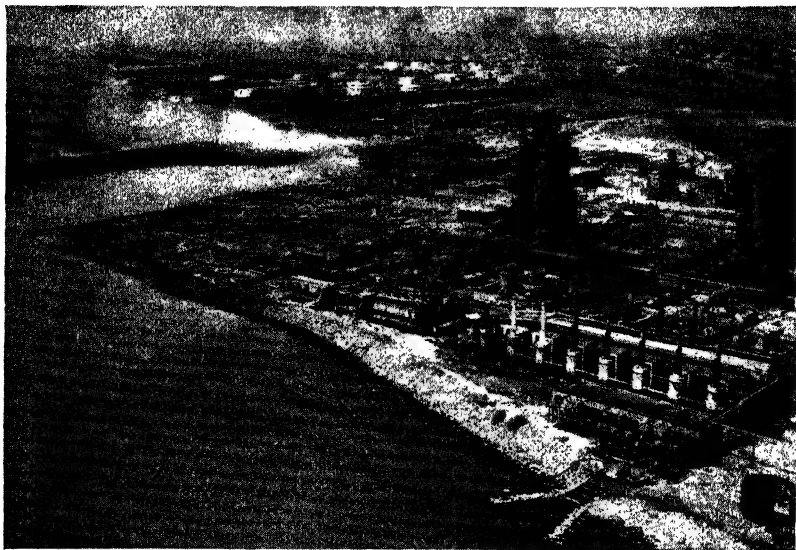
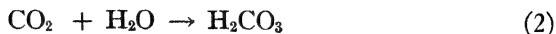
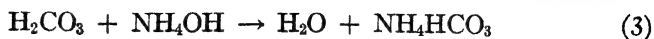


Figure 81. An aerial view of the Texas City water front three days after the ammonium nitrate explosion. The nineteen-million-dollar plant of The Monsanto Chemical Co. was entirely destroyed. (*Courtesy of Acme Newspictures.*)

The only raw materials actually consumed in this process are salt and limestone, and both of these are very inexpensive. The process may be illustrated most simply by imagining that ammonia gas and carbon dioxide gas are passed into a cold saturated salt solution. The reactions involved are simple ones. The ammonia and carbon dioxide react with the water to form a base and an acid, respectively.



The resulting acid and base react to form an acid salt (neutralization).



The acid salt (ammonium hydrogen carbonate) then reacts with the sodium chloride (metathesis),

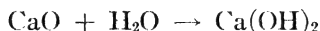


to form sodium bicarbonate and ammonium chloride. Since the NaHCO_3 is the least soluble product, it separates as a white crystalline solid, which is removed by filtration.

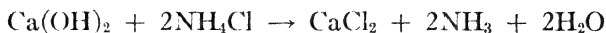
Carbon dioxide is needed for reaction (2), and it is produced by heating limestone,



and, as stated previously, the limestone is thus actually used up in the process. At the same time, quicklime is formed as an apparent by-product. It is only an apparent one because reaction (4) yields NH_4Cl and from this one needs to recover the ammonia for re-use. This is done by first treating the quicklime with water to form slaked lime,



and this in turn is used to recover the ammonia,



which is then put back into reaction (1). Thus, the limestone and the salt are in fact the only raw materials consumed, and calcium chloride is the only permanent by-product; there is always a market for it. The Solvay process proved to be so sound economically and of such high technical efficiency that processes previously used to produce sodium bicarbonate were unable to compete. Furthermore, the Solvay process provides the normal sodium carbonate by the simple procedure of heating the acid salt,



and the carbon dioxide thereby liberated is put back into the process via reaction (2), and again there is essentially no loss.

The normal sodium carbonate, Na_2CO_3 , is the commercial chemical, *soda ash*. In addition to the Solvay process, soda ash is manufactured by an electrolytic process, and occurs in nature as the mineral *trona*, $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$, and in several other forms as well. Im-

portant deposits are known in Africa, China, Siberia, Central Europe, and Central and South America. In the United States, the chief deposits are those at Searles and Owens Lakes in California and at Green River in Wyoming. From all sources, our domestic production of sodium carbonate (including exports) amounted to more than four

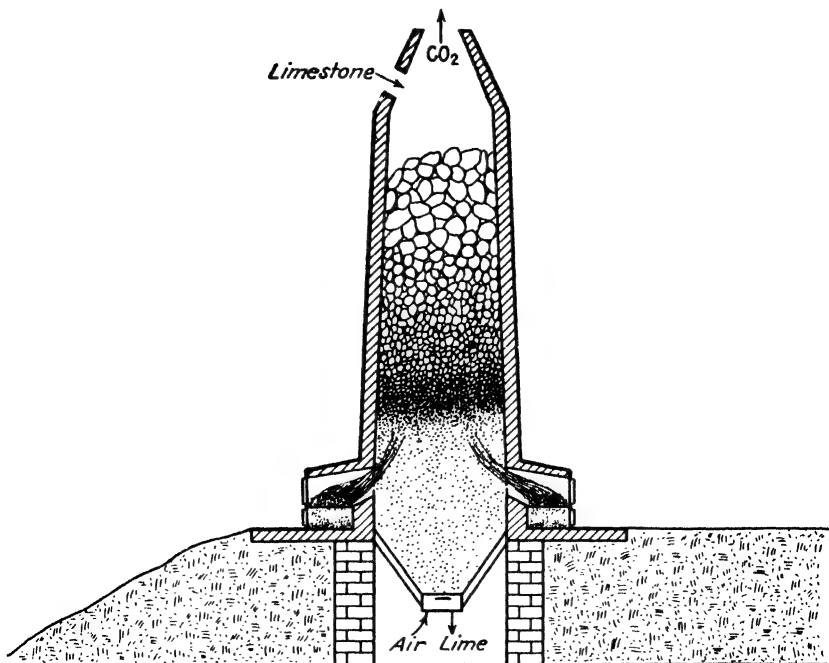


Figure 82. A limekiln.

and a half million tons in 1947, and production facilities are being expanded rapidly. This substance is sold in the form of soda ash, as *glassmaker's soda* ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$), and as *sal soda*, *washing soda*, or simply *soda* ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$). In its various forms, sodium carbonate is used in the manufacture of glass, soap, paper, textiles, and rubber. Other important uses include water treatment (the lime-soda process), the production of aluminum, and in the formation of a long list of other industrial chemicals. So much emphasis earlier in this chapter was placed upon the scale of production of sodium chloride that it is of interest to note that about half of our production of salt is used in the manufacture of sodium carbonate.

Calcium Carbonate. Vast and widely distributed natural supplies of this salt provide an almost inexhaustible supply of a cheap and useful raw material for industry. The mineral *calcite* is almost pure CaCO_3 . Other familiar forms include *marble*, dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$), and ordinary *limestone*. Oyster shells are used in industry as a source of CaCO_3 ; eggshells and coral are other materials having a high calcium carbonate content. Millions of tons of this salt are used annually in the United States, and it is widely distributed throughout the different geographical areas. The leading producers are Ohio, New York, Michigan, Illinois, and Pennsylvania.

TABLE 6. Salts and Their Uses

<i>Name</i>	<i>Formula</i>	<i>Uses</i>
Aluminum chloride	AlCl_3	As a catalyst. In the refining of petroleum
Strontium nitrate	$\text{Sr}(\text{NO}_3)_2$	Imparts the red color to signal flares and fireworks
Ammonium bicarbonate	NH_4HCO_3	Active ingredient in "smelling salts"
Sodium sulfide	Na_2S	Removes hair from hides (including that of human beings)
Sodium hydrogen sulfite	NaHSO_3	In manufacture of dyes and paper, and in tanning
Sodium sulfate (salt cake)	Na_2SO_4	In manufacture of glass, pottery, and paper
Sodium thiosulfate (hypo)	$\text{Na}_2\text{S}_2\text{O}_3$	In photography
Sodium perborate	NaBO_3	Antiseptic and bleaching agent
Calcium sulfate (plaster of Paris)	$(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$	Plaster casts, building material
Calcium sulfate (gypsum)	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	As a filler in paper; in manufacture of crayons; as a paint pigment
Magnesium sulfate (Epsom salts)	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	As a medicine. Used in dyeing and tanning and as a filler in cotton cloth
Potassium aluminum sulfate dodecahydrate (alum)	$\text{KAlSO}_4 \cdot 12\text{H}_2\text{O}$	In water treatment. Many minor uses

Marble and limestone are common materials used by the construction industries. The construction of highways and the manufacture of cement are other large consumers of limestone. Some is used as fertilizer, some in the metal industries, etc. From the standpoint of its use in the purely chemical industries, the production of lime and carbon dioxide is of major importance. Lime is produced by heating limestone

in large *kilns* (Fig. 82), and the resulting quicklime is either sold as such or converted to slaked lime.

Other Salts. Salts of silicic acid (the *silicates*) are included in Chapter 18, those of acids related to hydrochloric acid are discussed in Chapter 22, salts of organic acids are considered in Chapter 27, and the phosphates enter into the discussions in Chapter 31. In addition, a few other common salts and their uses are listed in Table 6.

EXERCISES

1. *New term:* metathesis (or metathetical reaction).
2. What states produce most of this country's supplies of sodium chloride?
3. Why do most of the salts discussed in this chapter not occur widely in nature?
4. Why is it that the utilization of a single chemical may serve as an index to business activity?
5. How do metathetical reactions differ from oxidation-reduction reactions?
6. Distinguish between baking soda, washing soda, glassmaker's soda, and soda ash.
7. What are some of the different forms in which calcium carbonate exists in nature?
8. How is salt produced from salt wells (include a suitable diagram of equipment)?
9. Give important uses for each of the following salts: NaHCO_3 , NaNO_3 , NaCl , CaCO_3 , KNO_3 , Na_2CO_3 , NH_4NO_3 .
10. How are the names of the different classes of salts derived?
11. What are some of the more important natural sources of sodium chloride?
12. Describe briefly the recovery of nitrate from *caliche*.
13. What is meant by the "solar salt industry"?
14. What materials would be needed (a) to start operation of the Solvay process; (b) to keep it in operation?
15. What is the distinction between saltpeter and Chile saltpeter?
16. Write an equation showing the formation of "laughing gas."

17. Write equations for the four principal reactions involved in the Solvay process.

COLLATERAL READING

ELDER, SCOTT, and KANDA: "Textbook of Chemistry," Harper & Brothers, New York, 1948, Chapter 16, pp. 212-219.

SCHOCH, FELSING, and WATT: "General Chemistry," McGraw-Hill Book Company, Inc., New York, 1946, Chapter XXXII.

The Evolution of Industrial Chemical Products and Processes

IT IS OFTEN proclaimed by leaders in science and industry that the lay public is unappreciative of the gains that accrue to modern society as a result of technological advances. It is said that the many new products which add to the comfort, convenience, or pleasure of living are too much taken for granted. Such statements are largely true, and for very good reasons. The very truth of these statements is an indirect tribute to modern technology. If new products or processes were rarities, every one of us would be much more impressed by them; as it is, they arise with such frequency that it is inevitable that we should come to consider them more or less to be expected in the normal course of events. Still another contributing factor merits attention. Even those who have studied chemistry and the related subjects in science and engineering are all too commonly just as poorly informed with respect to the "growing pains" of a new product or a new process. Every effort may be made by teachers to imbue the student with the technological elegance of some new development, and yet its metamorphosis is usually neglected entirely.

Accordingly, it is the purpose of the present discussion to trace briefly the evolution of chemical products and processes. Although appropriately limited to purely chemical industries, much that is included here applies also in broad outline to many non-chemical enterprises as well.

The Chemical Industries. At the outset it must be made clear that it is difficult to generalize with respect to industries so diverse as those typically classified as chemical. Nevertheless, they all possess certain common characteristics. They are all grounded in the same fundamental scientific principles even though they may differ in relation to their

scale of operation and the nature of the particular products that they make available. With but rare exceptions, they are all alike in that the profit motive is the reason for their existence. It is not inappropriate to paraphrase realistically a familiar advertising slogan so that it will read: "Better things for better living (and profits) through chemistry."

For present purposes we shall classify the chemical industries into three broad categories. The *heavy chemicals industries* are those engaged in the routine large-scale production of chemicals such as sulfur, sulfuric acid, ammonia, and numerous organic chemicals. These industries are characterized by large (tonnage) output and usually a low unit cost. The *fine chemicals industries*, or the producers of chemical specialties, are also purely chemical industries but are the ones concerned with production on a much more limited scale and at a higher unit cost. They appeal to a much more restricted market, and their operations are usually more flexible and more readily adaptable to new and/or changing trends in demand. In addition to these, there are numerous industries that should be classified as semi-chemical rather than strictly chemical. These include the petroleum, glass, rubber, iron and steel, and other industries in which chemistry plays an important but by no means a dominant role. In these industries, the chief concern is usually the fabrication of specific articles of commerce for the retail trade. There is certainly no intention to minimize the place of chemical science in these industries; rather it is intended to show a distinction between these and the industries that are concerned only with the production of chemicals, per se.

The nature and variety of the chemical and semi-chemical industries are such that they exert a profound influence upon the economy of this or any other country that enjoys any appreciable measure of industrialization. It is consequently important that any discussion of their products and processes should give due consideration to the attendant economic factors.

The Research Stage. The problem at hand is that of portraying the evolution of some chemical process or of some chemical product. We wish to show what went on behind the scenes, so to speak, in the days, months, or years preceding the time when the product was first offered for sale in the open market. This is indeed a large order, and one that can be treated here only on a brief and rather generalized basis.

Stories are always best recounted by starting at the beginning, but in the case of chemical research the true beginning may be obscure. We shall, however, start with the inception of the fundamental ideas that are behind successful process or product development and try to show the contribution made in the research laboratory. The word *research* is defined as a careful and diligent inquiry or thorough investi-

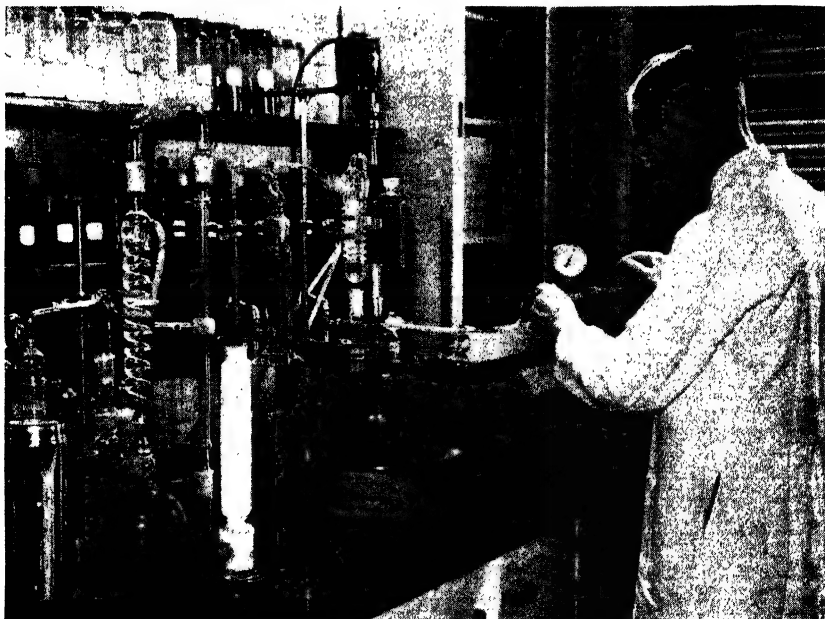


Figure 83. An industrial research laboratory. (Courtesy of Parke, Davis and Company, *Therapeutic Notes*.)

gation designed to provide new information. The word is derived from the Latin, *re-circare*, literally "to go around again." Any experienced research worker will freely admit that there is a true element of reality in the literal translation.

The research laboratory is a place for experimentation. Experiments however are based upon ideas, and these originate in the mind of man. Doctor C. F. Kettering of the General Motors Research Laboratories has expressed it well by the statement

There are many kinds of research, but when you get down below the surface, down to fundamentals, there is very little difference among them. In the final

analysis, research is a state of mind. The problems are going to be solved in somebody's head.

It is of course difficult to trace the origin of ideas, still more difficult to evaluate the degree to which a particular idea involves true originality, and next to impossible to predict whether any idea will prove to be a practical one.

Chemists have a well-established practice of recording in their professional literature the results of all kinds of experiments. These results need not be in any way useful; all that is required is that they provide new knowledge. Many of the best ideas for new experiments come from reading this accumulated literature and coming across isolated pieces of information which suggest an interesting experiment or piecing together apparently unrelated facts in a manner such that they lead to some novel idea which could not have arisen from any single fact. Perhaps these points may be made clearer by a specific example.

Let us suppose that, in the course of reading some of the older chemical literature, a chemist's attention is attracted to a compound first prepared many years ago but thereafter not studied further. The chemist reads over the directions for the preparation of this compound and recognizes that one or more of the necessary reactants has recently become readily available and at low cost. Furthermore, the formula of the compound suggests that it might be useful as an insecticide, as a medicine, or for some other purpose. As a result of this or some other combination of circumstances, the chemist sets out to study this compound from the standpoint of methods for its preparation, of its properties, and of its possible uses. All of the knowledge accumulated in the course of the chemist's training and experience is brought to bear upon the problem of planning an appropriate program of research. Possibly the first thing to be done is to prepare a sample of the compound by the known method. (It should also be noted that chemists often set for themselves the task of preparing new compounds for which no methods of preparation are known.) If preliminary studies of the properties of the compound show that it might be useful, other methods for its preparation may be devised and one of these methods will be selected for more detailed study. This selection is based upon the availability and cost of the reactants used and the "yields" and purity of the desired product that are provided by the different methods. By some such sequence of events, the chemist will become convinced that

he has at hand a reaction suitable for the preparation of the compound and that the compound is potentially useful. It is important now to keep in mind that, in the conduct of the research up to this point, the chemist has been drawing (and later will continue to draw) upon the accumulation of scientific and technological information which represents the work of generations of scientists.

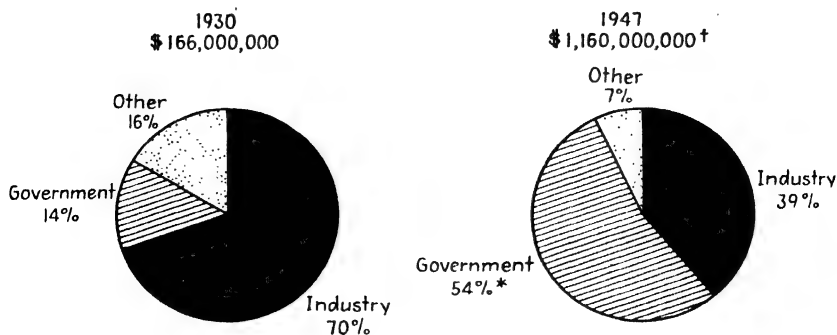
It may be assumed that the compound and its method of preparation appear to be feasible from the standpoint of the chemistry involved; further research will probably depend upon market possibilities. It is not necessary that a market exist; there is always the possibility that a market can be created. In any event, an existent or potential market for the compound is all that is needed to justify additional research.

One then enters upon the process-development stage of the research, and it is in this stage that process feasibility must be demonstrated. The chemical reaction or reactions are studied intensively, and all variables such as concentration, temperature, time, catalysis, etc., are investigated with a view to the establishment of an optimum set of experimental conditions. This may be accomplished quickly, or it may require months, or even years, of work.

It is not possible in a discussion of this sort to delineate any fixed pattern of developments. Anyone who has been engaged in industrial chemical research may argue with justification that the sequence of developments outlined in the preceding paragraphs is not typical. The simple fact is that there is no such thing as a *typical* pattern for the conduct of research. The point is, however, that considerable variation in practice occurs at the point at which the technical feasibility of the process has been demonstrated in the laboratory. In order to simplify this discussion, it will be assumed that all of the laboratory work has been done on a scale so small that no significant quantities of the compound have been produced. This means that the consideration of economic feasibility must await somewhat larger scale operation in the so-called pilot-plant, or semi-works, stage.

It requires no great insight to lead one to the conclusion that even the small-scale operations that typify research-laboratory experiments cost much money. Prior to World War II, most of the money expended for research originated in the chemical industries and represented their investment in the future. In the year 1947, however, more than half

of the expenditures for research represented funds from the various governmental agencies. The marked change during the war period is shown by Fig. 84, which shows also that in 1947 expenditures for research reached an all-time high estimated at \$1,160,000,000. A few comments about research activities in colleges, universities, and privately endowed research institutions are not out of place here. It is



* Four-fifths by Army and Navy, one-fifth by other Government agencies

† Excluding atomic energy expenditures

SOURCE: Report of President's Scientific Research Board

Figure 84. Expenditures for research in the United States. (Courtesy of *Chemical and Engineering News*.)

generally but not universally true that research institutions supported by private philanthropies are the places where the profit motive receives the least consideration and humanitarian motives are in the foreground. Research foundations maintained for the study of problems in human nutrition, the causes and possible cures for cancer, etc., are typical examples.

Research conducted in college and university laboratories falls in a somewhat different category and is of interest because of trends that have developed within the last few years. That research programs should be maintained in these institutions is not even debatable. It is axiomatic that educational institutions should not only impart knowledge but make additions to it. In addition, it is only through the maintenance of active research programs that schools may provide advanced training for those who wish to prepare for careers in research work. It has been historically traditional that colleges and universities should concern themselves only with what has come to

be called "pure research." That is, studies should be pursued for the sheer satisfaction of accumulating new knowledge, and research conducted with a view to practical applications should be left to private enterprise. Thus a fairly sharp line of demarcation between academic and industrial research prevailed for a long time, and the "ivory-tower" concept of the former became firmly established. This situation has changed rather drastically in the last two decades. Both academic and industrial institutions have come more and more to the realization that this kind of stratification is disadvantageous to all concerned. Industries have moved in the direction of providing financial and other support for research in colleges and universities, and these in turn have come to look with favor (or at least to tolerate) research of somewhat more practical character. At the same time, more work of a purely fundamental nature is being done in industrial laboratories. Support of research by government agencies has also had a profound influence upon research in educational institutions. The increased participation in research by the government (Fig. 84) has been felt in academic circles, not so much because it has changed the objectives of research effort, but rather because it has led to a marked increase in the amount of research accomplished.

The Pilot-plant Stage. Let us now return to the chemical process for the production of a potentially useful compound and recall that it had passed through the laboratory-scale research stage and was ready for studies conducted on a somewhat larger scale. It is at this point that economic factors loom large. The research costs mount rapidly as the scale of operation is increased, and management becomes increasingly cautious about authorizing large capital investments for continued process-development work unless the prospects for success are reasonably good. There are, of course, a few notable exceptions. In times of national emergency, the government may underwrite research and development programs such as those pursued during World War II in connection with synthetic rubber, penicillin, and the utilization of nuclear energy. In these cases, the economic rules of the game are suspended, and cost factors are given little if any consideration.

When a process is carried from the research laboratory to the pilot plant, it enters an area of cooperation between the research chemist and the chemical engineer. Both contribute to this stage in the development of the process, and they usually continue to work cooperatively

until the process becomes well established in the full-scale manufacturing plant.

The pilot plant is essentially a miniature manufacturing plant in which one can carry out the necessary chemical reactions on a scale intermediate between the research laboratory and the full-scale plant.



Figure 85. Pilot-plant for the production of glycerine from petroleum. (Courtesy of Shell Development Co.)

Oddly enough, some reactions that take place satisfactorily on a small scale prove to be unsuited to large-scale operation. Others behave equally well on a large scale, and some actually proceed better. The success or failure of the entire venture is usually spelled out in the results of pilot-plant tests. Here one must evaluate the performance of materials for the construction of equipment, train personnel to operate the equipment, and secure cost data and engineering data that will serve as a basis for decisions relative to the feasibility of a still larger scale of operation. The cost and availability of raw materials become matters of prime importance, and attention is given to prob-

lems of safety, waste disposal, by-product utilization, etc. At the same time, pilot-plant operations provide large enough quantities of the compound so that market research studies may be initiated.¹ The compound is tested exhaustively in the hope of finding new uses and thus new market outlets. Samples are distributed to potential customers in order that they may determine whether they are interested in having still larger quantities made available for their use. Advertising programs are initiated, technical information is disseminated, the overall competitive picture is reviewed, and price policies are largely established. It is at this stage that both technical and economic feasibility must be clearly established because the decision to proceed into full plant-scale operation is the one that commits heavy investments of venture capital.

While the process is still in the pilot-plant stage, the need for additional research often arises. Unforeseen difficulties may require that alternate procedures be devised, and numerous ways of improving the process are often discovered by either the chemist or the engineer.

Plant-scale Operation. On the assumption that we are concerned with a process for use by one of the heavy chemicals industries, it is helpful to think of the various evolutionary stages in terms of comparative quantities of the compound produced. We may adopt the idea that the research laboratory produces *grams*, the pilot plant provides *pounds*, and the manufacturing plant supplies *tons* or *carloads*. In many of the fine chemicals industries, pounds represent the upper limit in the scale of profitable levels of production.

If the chemical process in question warrants the construction of a full-scale manufacturing plant, its location is a decision of major importance and one that must be made in the light of many determining factors. One must consider a possible geographical location in relation to the location of raw materials and market. It must be decided whether it would be cheaper to locate the plant near the existing market and transport the raw materials or to locate the plant near the source of supply of the latter and transport the manufactured product. The nature and relative cost of the available forms of transportation must always enter into these deliberations. The availability of water sup-

¹ In many cases, these studies are begun using material produced while the process is still in the laboratory research and development stage.

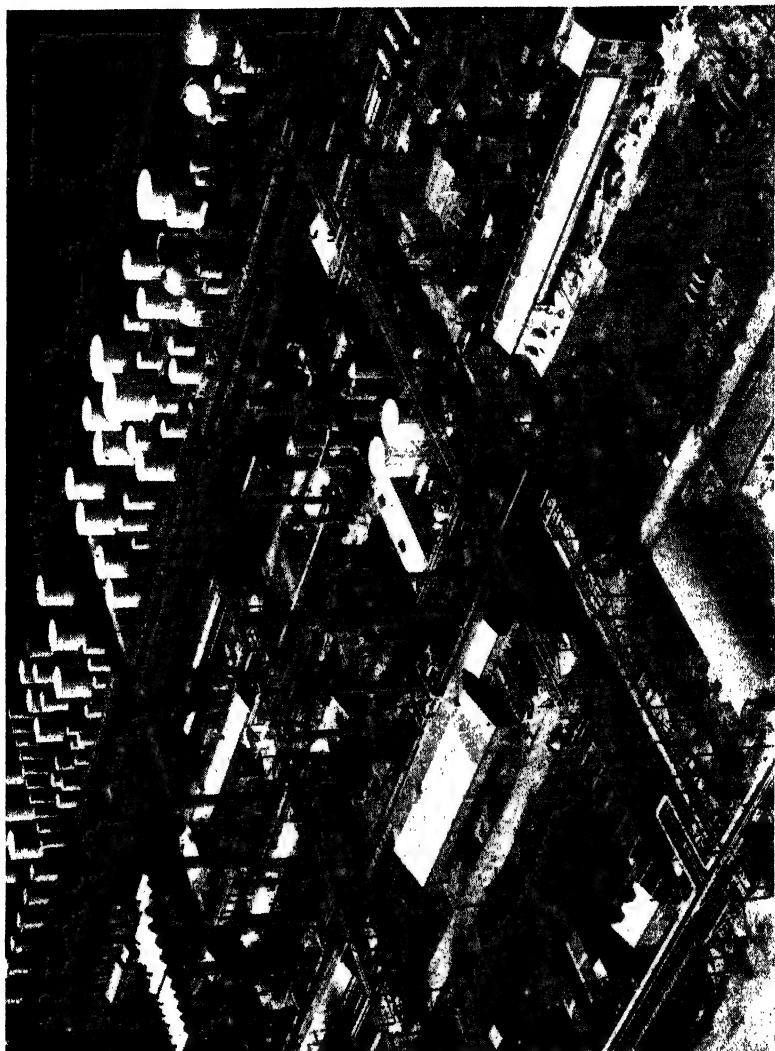


Figure 86. An aerial view of a chemical plant used for the production of glycerine from petroleum.
(Courtesy of the Shell Chemical Corporation.)

plies for use either directly in the chemical reactions or as a heat-exchange medium is often a factor of major concern.

Some additional factors include the availability of labor and the relative strength of labor organizations in the particular area under survey. It must be kept in mind that the chemical industries employ a high proportion of skilled or at least semi-skilled labor, and one must make certain that it will be possible to recruit an operating staff. The very feasibility of the entire venture may hinge upon local, state, and national taxation policies. The impact of taxation upon the establishment of new industrial plants is clearly indicated in a report issued in England by the Machinery and Allied Products Institute:

That some features of British tax structure have contributed to technological decay hardly admits of doubt. Ever since World War I, taxation has fallen with extreme gravity on those sectors of the national income that supply the capital funds of industry, especially its risk capital.

Once the manufacturing plant has been built and placed in operation, much additional chemical work remains to be done. Chemical analyses of the plant product must be made on a routine basis to ensure uniformity in the performance of the process and the quality of the product. Additional research programs are undertaken for the purpose of improving the technical features of the process and lowering the unit cost of the product, or both.

Particularly during the early stages of plant or even pilot-plant operation, the balance between price and volume of sales must be studied carefully. If one can produce the compound at a cost of 40¢ per pound and sell it profitably at 50¢ per pound, might it not be more profitable in the long run to lower the price to 30¢ per pound (*i.e.*, below the existing production cost) and thus hope to expand the sales so greatly that the unit cost of production may be brought well below 30¢ per pound? This sort of practice is not uncommon in the chemical industries, and it of course leads to lower prices to the ultimate consumer.

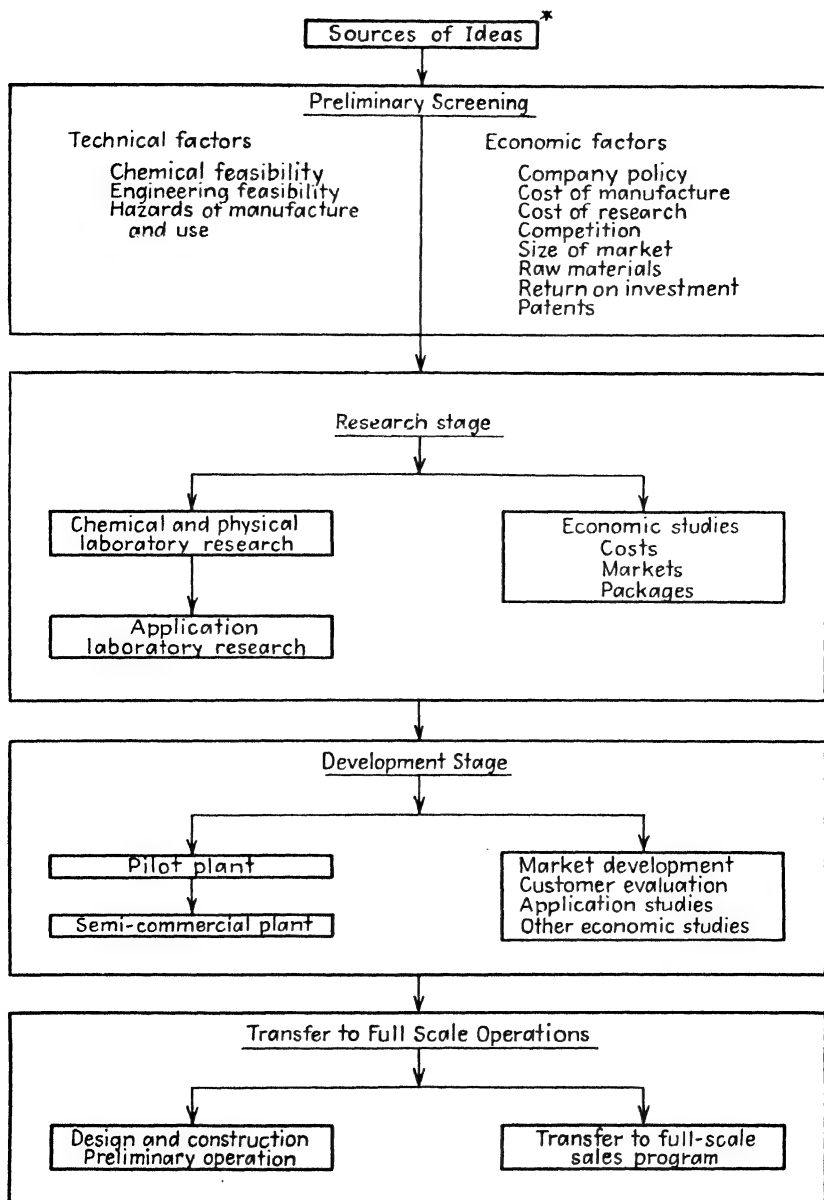
Whatever approach may be employed, it is true that the history of the chemical industries is one of steadily decreasing prices coupled with steadily increasing rate of production. Although there have been other contributing factors, these price trends have reflected improvements in methods and operating efficiency resulting from active and intelligently planned programs of scientific research. The first peni-

cillin that became available had to be priced so high that its use was prohibitively costly except in cases of extreme need. As research laboratories proceeded to learn more and more about this substance, it became possible to devise progressively improved methods of production and this trend continued until the unit cost became relatively so low that penicillin is now not even considered to be a particularly expensive medicinal.

One of the purposes of the preceding discussion has been to show the inseparability of technical and economic considerations during the normal progress of new product development in the chemical industries. These relationships are emphasized in summary form by the chart that follows.

Patents. While it is beyond the scope of this book to indulge in any detailed discussion of patents and patent policies, there are certain pertinent facts that should not be omitted entirely. The purpose of our patent system is to provide an equitable measure of protection for the investments that are made in the course of development of new products or processes. If there were no such system of protection, those who seek to establish new enterprises would have to depend upon two unsatisfactory alternatives. They would have to make a choice between being uncertain of their ability to maintain in strict secrecy all details of any new product and its method of production or being faced with the possibility of ruinous competition. If Company *A* invests a million dollars in the development of a new product and Company *B* is free to produce the same product in the same way without having to amortize any investment in research and development, the competitive disadvantage that would accrue to Company *A* is not difficult to forecast.

In order to be patentable, a product or process must be new; it must not have been known or practiced previously. In addition, that on which patent protection is sought must be useful. It is obvious that the words *novelty* and *utility* are relative terms, and therein lie many of the trials and tribulations encountered by the Patent Office, those who apply for patents, and the legal representatives of both. One may not obtain a patent on an idea or on any natural phenomenon. Interestingly enough, one may, however, secure a patent on a rosebush provided that it is one having characteristic qualities which have been induced by selective breeding or cultivation.



* Courtesy Chemical and Metallurgical Engineering

When and if a patent is granted, protection is provided for a period of 17 years. There are several ways in which the effective life of a patent may be extended, but the most common is the procurement of patents on improvements which are made in the originally patented process. These arise as results of research. During the effective life of a patent, its owner may elect exclusive use or may choose to license others to produce the same product or use the patented process in return for an appropriate fee or royalty paid by the licensee.

It will be noted that the present and necessarily all too brief discussion has included nothing about the procedures followed in the application for and procurement of patents or about many of the practices indulged in by those who hold legally constituted patent protection. The subject of patents is a large and very controversial one. For those who wish to learn more about the subject, it is recommended that books on patent laws and procedures be consulted.

EXERCISES

1. *New terms:* heavy chemicals industries, fine chemicals industries, semi-chemical industries, pilot plant, research.
2. What features are necessary to a patentable invention?
3. Indicate briefly the comparative scale of operation in the research laboratory, the pilot plant, and the manufacturing plant.
4. What are some of the factors to be considered in the choice of a location for a chemicals-manufacturing plant?
5. What procedures are used in attempting to evaluate the potential market for a new chemical product?
6. What is the purpose of patent protection?
7. Cite at least one good reason why an increased scale of production should lead to a decrease in the unit cost of the product.
8. Give some good reasons why steel mills that utilize Minnesota iron ore are located in places such as Gary, Ind., and Pittsburgh, Pa., rather than in Kansas and Nebraska.
9. In recent years there has been a decided trend toward locating chemicals-manufacturing plants in the South generally and more particularly along the Texas Gulf coast. Suggest some reasons for this trend.

10. Why should research work on a chemical process continue long after the successful demonstration of its operation in a full-scale manufacturing plant?

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BIESTERFELD: "Patent Law for Chemists, Engineers, and Students," John Wiley & Sons, Inc., New York, 1943.

WEIDLEIN and HAMOR: "Glances at Industrial Research," Reinhold Publishing Corporation, New York, 1936.

The Ceramic Industries

THE CERAMIC industries are those which use silica (SiO_2) or silicates (salts of the silicic acids) as raw materials. Their products include glass from silica, and pottery, porcelain, enamels, terra cotta, brick, tile, cement, and many similar items from various materials such as clay, kaolin, feldspar, and other natural or artificial silicates. Owing to the availability of the raw materials and the ease with which they can be worked, ceramic articles have been made from the earliest times, and their production still constitutes an important example of the chemical arts.

Glass. The term *glass* is a fairly general one, referring to any material that on changing from the liquid state to the solid state does so without crystallizing, yet becomes a rigid body. Glasses are sometimes referred to as supercooled liquids because of their lack of crystalline structure and their ability to flow if sufficient pressure is applied over a long period of time. The general definition of glass includes many substances that are too specialized for inclusion in this book. For our purposes we shall use the term *glass* to mean a mixture of various silicates, together with an excess of silica, *i.e.*, the ordinary commercial varieties of glass.

The importance of glass in our way of life is frequently overlooked because of its abundance, low cost, and unobtrusiveness. Without glass or a similar material the work of factories would be dependent upon the weather and the time of year, and this would greatly increase the cost of their products. Our homes would be without electric lights or even lamplight, and hence it would be very difficult to read or study at night, with a resulting lack of accomplishment. The microscope is dependent upon glass, and without the microscope progress in medicine and allied fields would be materially reduced. It is fortunate that essentially all countries have the necessary raw materials for the pro-

duction of glass, and the world has been enjoying its use for many centuries.

The history of glass dates back to the First Egyptian Dynasty (5000 B.C.), and the art of glassmaking may be even older, for no one knows how it originated. The very first glass was probably of natural origin, found in lava beds. This naturally occurring glass is called *obsidian* or volcanic glass; a well-known deposit is that in Yellowstone National Park. Obsidian was used by the American Indians for arrow-heads, spears, razors, etc., and it was an article of commerce in other countries as early as the Bronze Age.

The earliest examples of manufactured glass come from the Nile Valley, probably due to both the advanced civilization of the Egyptians and the availability of the necessary sand (silica) from the banks of the Nile and the required alkali from the nearby deserts. The Egyptians first used glass to glaze pottery, then later for the production of beads and pendants designed to replace or imitate natural precious stones. It is evident that objects of glass were made at least as early as 1490 B.C., for there exists a glass goblet with that date on it and bearing the name of the current Pharaoh. The chemical analysis of this glass is almost identical with that of modern window glass. Glass tear bottles, or lachrymatories, have been found in tombs dating from 4700 B.C.; they seem to have served no useful purpose other than to catch a few well-chosen tears.

The art of glass blowing dates from about 250 B.C. and was well developed by the time Caesar Augustus conquered Egypt in 23 B.C. The Egyptians were required to pay their taxes to Rome in glassware, and many of their better artisans were persuaded to move there, also. The glass made during this period was used for dishes and mosaic floors; a small amount was used for windows, although the glass was translucent and not transparent.

By A.D. 1200 the Venetian glassmakers had learned how to make clear, transparent glass, which was used for mirrors and ornamental objects. Their secrets were so valuable that the workers were confined on an island (Murano), and their emigration was prohibited under penalty of death. The crystal glass of Venice and the colored glasses of France and England produced during the Middle Ages have scarcely been surpassed even by the most modern methods, for in that early period working with glass was an art practiced by artists. In 1557,

window glass was being made in England, and from that time on glass was esteemed more for its utility than for its beauty.

The first chemical industry started in this country was a glassworks in Jamestown, Va., in 1608. Beads, bottles, and trinkets were manufactured for barter with the Indians.

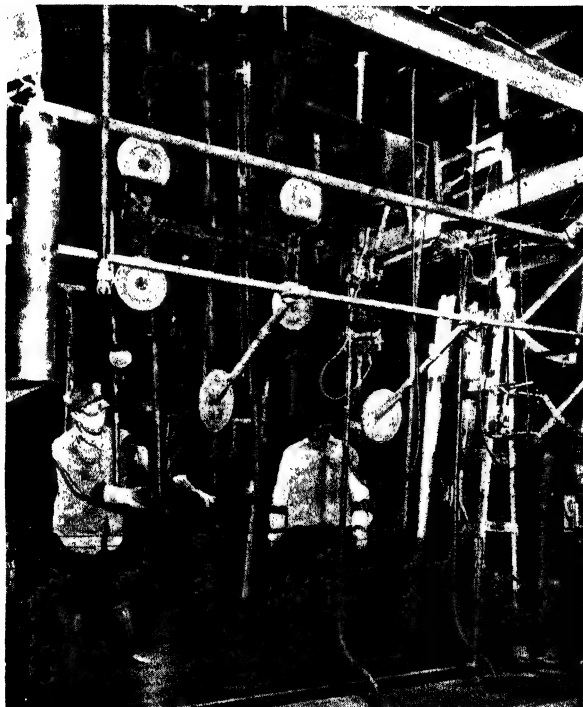


Figure 87. Window glass being cut after passing through smoothing and cooling rollers. (Courtesy of the Pittsburgh Plate Glass Co.)

The development of the glass industry has been more a matter of chance than experimentation. Within recent years, however, the scientist has been called in for advice, with the result that many new glasses for special purposes are now available.

Glass may be classified according to either its chemical composition or its use. Both classifications are used extensively, and both are useful. For our purposes the various glasses will be referred to in most cases by both their composition and their use.

Lime glass is the ordinary glass of windowpanes, bottles, glass brick, tableware, etc., and constitutes about 90 per cent of the glass produced. The basic materials for glass of this type are sand (silica, SiO_2), soda (sodium carbonate, Na_2CO_3), and limestone (calcium carbonate, CaCO_3).

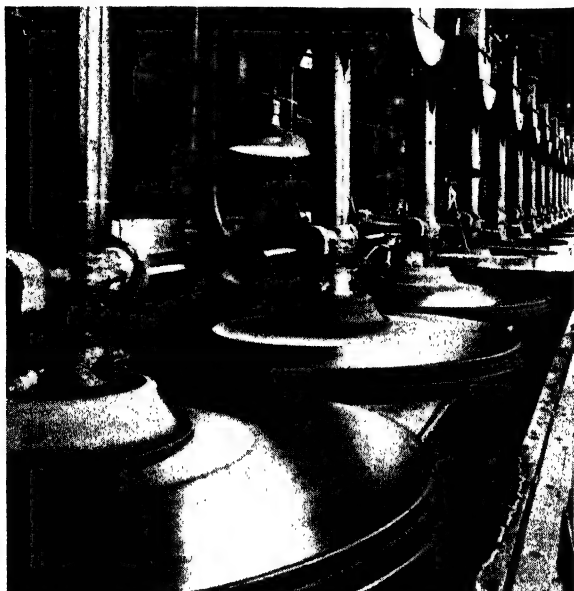
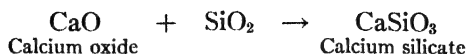
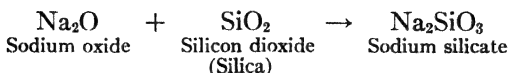


Figure 88. A battery of discs which are grinding and polishing plate glass. The glass moves under these discs at the rate of five feet a minute. (Courtesy of the Pittsburgh Plate Glass Co.)

These materials, plus a quantity of scrap glass added to lower the melting point of the mixture, are melted in "tanks" holding as much as 3 million pounds. Carbon dioxide is first driven off, and sodium oxide (Na_2O) and calcium oxide (lime, CaO) are formed. These metal oxides (basic oxides) react with the non-metal oxide silica (an acidic oxide) and form the metal silicates (salts).



The resultant mixture of sodium and calcium silicates along with an excess of silica constitutes glass. Because glass is a mixture, no formula can be written for it and its composition can be varied within fairly wide limits. Based on the raw materials, a typical window glass con-



Figure 89. This mirror was made from the first piece of plate glass made commercially in the United States. (*Courtesy of the Wyandotte Chemicals Corporation.*)

tains about 69 per cent silica, 9 per cent lime, 18 per cent soda, and 4 per cent of compounds of various metals.

Window glass is made, for example, by dipping a bar of steel three inches wide by six feet long in the molten glass and drawing the bar upward along with a thin sheet of glass. This glass passes through rollers, where it is smoothed and cooled (Fig. 87). The cooled sheet of glass is then cut to desired sizes, reheated, and then very slowly cooled (annealed) to avoid stresses and strains, which cause glass to crack easily. It has been said that enough window glass is produced each year to make an eight-lane highway around the earth at the equator.

Plate glass is made by pouring the molten glass onto a wide, flat iron surface and rolling the glass to the desired thickness while it is still plastic. After annealing, the sheet of glass is ground and polished with rouge (Fe_2O_3) (Fig. 88) to give a flat surface free from distortion. A variation in this method of producing plate glass is to allow the

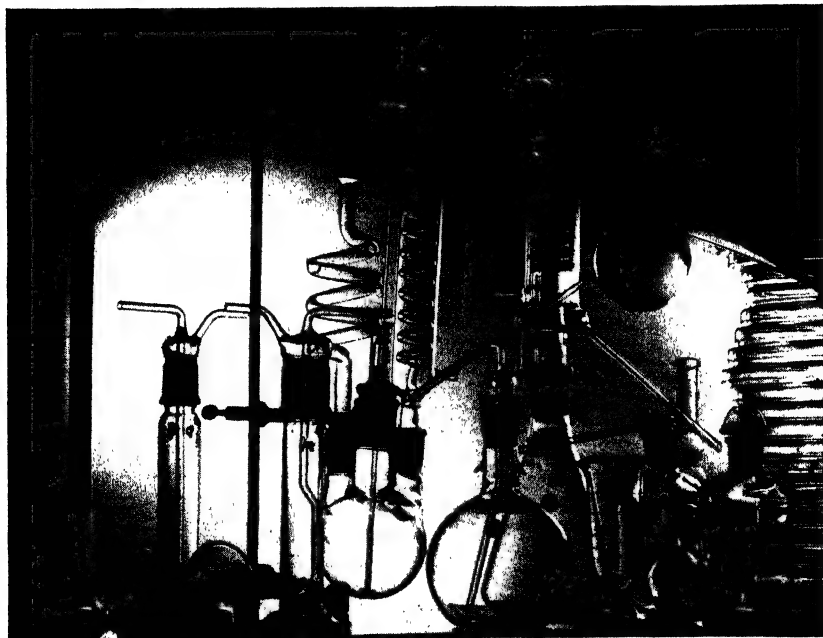


Figure 90. Some typical laboratory glassware made from Pyrex. (Courtesy of the Corning Glass Works.)

melted glass to flow on a revolving drum and then pass under a roller and finally to be cut into sheets and processed as usual. The first piece of plate glass made commercially in this country was made by J. B. Ford in 1870; this glass is now a mirror in his granddaughter's home (Fig. 89).

Glass *bottles* and similar objects are made by blowing the glass into molds of the desired shape. In the past this was done by lung power, but now machines are used that can make as many as 100,000 bottles a day or electric-light bulbs faster than one can count them. Special patterns made in small quantities are still made by hand. Glass building blocks, dishes, automobile headlights, etc., are cast in molds or stamped

with dies. Glass bricks for use as building material have the twofold advantage of being able to admit light and also to insulate because of the enclosed air in their hollow centers.

Colored Glass. Many different colors can be imparted to glass by adding very small amounts of the appropriate metal in the form of its oxide. For example, cobalt and nickel oxides will color the glass purple; copper or chromium will give a green color, carbon or iron produces a yellow glass; and cuprous oxide, very finely divided gold, and selenium all impart a ruby-red color to glass. The selenium colored glass is used in automobile taillights and traffic signals. White or opal glass is made by adding phosphates or fluorides, and it is used for lighting fixtures, tableware, and decorative building panels. The green color of most common glass is caused by the presence of iron that was in the sand as an impurity.

Glasses for special purposes can be made by substituting different metals for the sodium and calcium in ordinary glass.

The most familiar of these glasses are the *borosilicate glasses* sold under the trade name of *Pyrex* (1915). Pyrex contains about 80 per cent silica, 13 per cent boric oxide (B_2O_3), and a smaller amount of sodium and aluminum oxides—in the form of silicates. These glasses are noted for their resistance to chemicals and high melting point, and they expand only slightly when heated. This last property permits the use of Pyrex over a direct flame without danger of cracking. All of these features



Figure 91. A Steuben glass vase showing Paul Revere, founder of the malleable copper industry in the United States. (Courtesy of the Corning Glass Works.)

account for the wide use of Pyrex glassware in industry and in chemical laboratories (Fig. 90) and for cooking utensils.

Flint, or *lead*, *glass* contains a high percentage of lead silicate and has a low melting point and high electrical resistance. It is used in the production of the 2 billion light bulbs and nearly all of the neon-sign tubing produced annually in the United States. It also has a high index of refraction and brilliance that makes it valuable for the production of cut glass and other art objects. The famed Steuben glass (Fig. 91) is of this type, as well as most simulated jewels (paste). Although most glass is used for industrial, scientific, and other utilitarian purposes, in recent years there has been a return to glass as a medium for artistic expression. Designed by prominent artists and engraved by craftsmen (Fig. 92), Steuben glass is treasured by connoisseurs of fine art.¹

Optical glass is a lead glass to which has been added a number of chemicals, including barium, aluminum, boron, and zinc oxides. This glass is used in the lenses of telescopes, microscopes, cameras, and eye glasses.

Ordinary glass has been modified in many ways to make it more suitable for some particular use. One of the most significant advances for the protection of the traveling public was the development of safety glass. *Safety glass* is made by sealing two sheets of plate glass together with a thin layer of organic plastic material. The plastic interlayer holds together and stretches under the blow and at the same time prevents the broken pieces of glass from flying about and cutting people. This ability of safety glass to yield under a destructive blow lessens the severity of the impact to a person thrown against it in an accident.

When wire is embedded in the glass, there is produced *wire glass*, which is used for factory windows and skylights. It is characterized by its resistance to shattering, and if the glass softens during a fire the wire holds it together and prevents destruction of the window. *Invisible glass* is made by coating the surface of the glass with an exceedingly thin film of certain metal fluorides. Glass of this type is used in store windows and showcases. *Tempered glass* is produced by

¹ Indicative of the growing appreciation of Steuben glass is the fact that the President of the United States chose a piece of this glass as a gift to the Princess Elizabeth of England on the occasion of her wedding.

suddenly chilling hot plate glass by a stream of air. It is about five times as strong as plate glass, is more flexible, and has the added advantage of crumbling rather than shattering or splintering when broken. Tempered glass is used to make *bullet-proof glass*.



Figure 92. A craftsman engraving a design on a Steuben glass bowl. (Courtesy of the Corning Glass Works.)

Very fine fibers of glass are obtained when molten glass is blown by steam through small orifices at the rate of two miles per minute. The average diameter of these fibers is about one-fourth that of human hair, but some as fine as one-twentieth the size of hair have been made. Two pounds of this fiber would be sufficient to reach around the earth. *Fiber glass* has many uses, most of which are dependent upon its flexibility, stability, and insulating properties. It is widely used for insulat-

ing aircraft, battleships, etc., where lightness is of paramount importance. Four inches of glass wool has the insulating power of ten feet of concrete. Glass fiber woven into cloth is used for window drapes, theater curtains, and filter cloth, but glass fabrics are not used extensively for clothing because it is slightly irritating to the skin. "Itching powder" is frequently composed of short pieces of glass fiber.

Water glass (sodium silicate) is made from silica and sodium carbonate. It differs from the glass thus far discussed in that it is soluble in water and therefore may be used in the form of a water solution. When the water evaporates, a brittle, glassy solid is formed. Water glass is the cheapest glue and is used to make cardboard shipping boxes, which are made up of layers of paper glued together. It is also used to fireproof wood, cloth, and paper, as a filler and binder in cheap soap, and to preserve eggs.

In 1947 the 600-million-dollar glass industry produced, among other things, over 250,000,000 square feet of plate glass, nearly 17 billion bottles and jars, and 840 million common water glasses.

Pottery. The manufacture of pottery, brick, and related articles is an industry even older than that of glassmaking. One of the reasons for this is that, while glass requires the high-temperature formation of silicates from silica and other materials by a chemical reaction, opaque ceramic articles are shaped from natural silicates and simply sun-dried or baked to bring about a change in physical structure.

The basic raw material used in the manufacture of pottery, etc., is clay. This *clay* has a variable composition but usually comes from the weathering of feldspar (KAlSi_3O_8). The purest clay (*kaolin*, or *China clay*) is white, and its formula may be represented as $\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9$. Most clays, however, contain such impurities as silica, undecomposed feldspar, and iron compounds, the latter being the material that gives common clay its color.

For a clay to be useful in the ceramic industry it must be able to become plastic when wet, thus permitting it to be shaped on a potter's wheel (Fig. 93) or pressed into a mold. The clay must also retain its given shape during the process of firing. Not all clays have these properties. Georgia and Florida have the best deposits of China clay in the United States.

The cruder forms of clay products, *brick*, *terra cotta*, *stoneware*, and *drain tile*, have very little chemistry associated with their manufacture.

Rather impure clay is molded into the desired shape, dried, and then fired in a kiln at a temperature sufficient to melt some of the impurities, which then act as a binder for the clay particles. The red color of these articles results from the fact that the usually pale-colored iron compounds in the clay are changed to red compounds by oxidation. *Fire-*



Figure 93. Forming the back of a plate on a potter's wheel or "jigger." (Courtesy of the Ceramic Industry Publications.)

brick is made from clay that is purer and consequently able to withstand higher temperatures without fusing. *Vitrified brick* is made at a temperature sufficiently high to cause a partial fusion of the clay with the resultant formation of a glass.

Chinaware is made from the finest white clay and feldspar. The various types of chinaware and earthenware are processed in slightly different ways, but they all go through the following essential steps: (1) shaping and firing; (2) glazing; (3) decoration. The wet clay ("slips") is molded on the potter's wheel, or "jigger," and then is partly dried before being placed in the kiln. In the kiln the object is

baked at about 1200° , and a 10 per cent shrinkage takes place (Fig. 94). The article that comes from the kiln is called *bisque* and is porous. Because of its porous structure the bisque must be glazed to make it non-absorbent and to give it a smooth surface.

Glazing consists in coating the surface of the object with a paste of fusible material, then reheating it until the glaze melts and flows over the surface. The constituents of the glaze may be silica, feldspar, various metal oxides, and borax. One of the greatest difficulties is to obtain a glaze that will expand and contract with changes in temperature

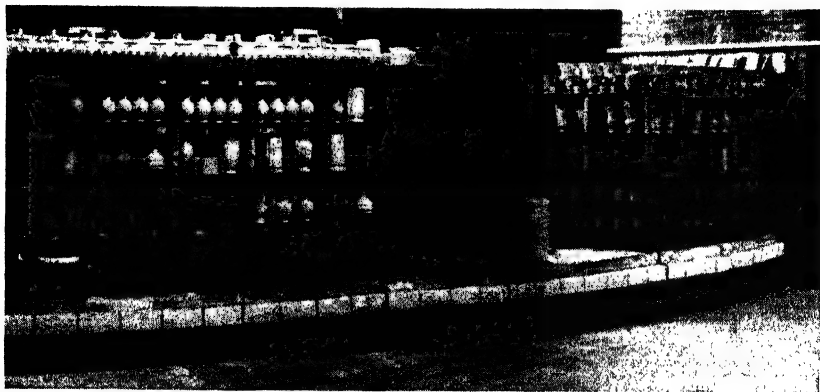


Figure 94. Ceramic objects entering kiln for baking. (Courtesy of the Ceramic Industry Publications.)

exactly to the same extent as the object being glazed; if this is not achieved, the glaze will crack. The cheaper varieties of ceramic products are glazed by coating the surface with salt. When heated, the salt reacts with the hot clay to form sodium aluminum silicate, which cools to give an impervious coating.

If a color or design is desired, the design may be painted on the article with metal oxides before glazing or it may be painted on the glaze and the article then fired again to melt the design into the glaze (Fig. 95). If the article has already been glazed, the pigments frequently used for the design are colored glasses.

Porcelain is made from a mixture of kaolin and feldspar. The feldspar fuses, binds the kaolin particles, and makes the article translucent. The article is then dipped in a water suspension of powdered feldspar and fired again to impart a glaze.

When the same type of material that is used for glazing chinaware is fused onto a metal surface, the resultant product is called *enamel*. The enamel is made by first fusing together feldspar, silica, fluorspar, cryolite, and other chemicals. This material, called "frit," is pulverized, made into a paste, and applied to the metal surface, where it is baked on; several coats of enamel are usually applied. It is used on granite-

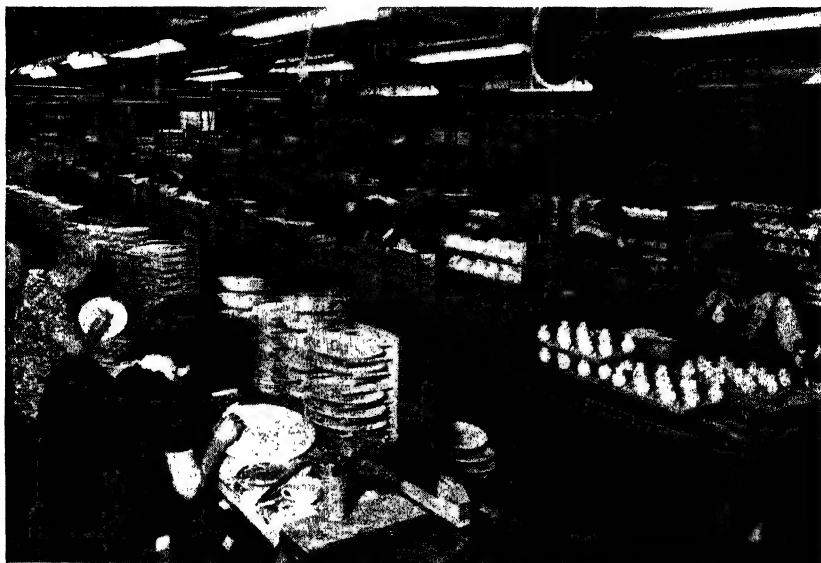


Figure 95. Decorating various ceramic objects. (Courtesy of the Ceramic Industry Publications.)

ware cooking utensils, bathtubs, refrigerators, stoves, etc., to make these objects look like porcelain and to protect the surface from rust and chemical action. Enamel has many of the properties of glass and should be treated accordingly.

Cement. Cement is a fine gray powder composed of silicates and basic oxides and is characterized by its ability to harden under water as well as in the air. Materials of this type have been used for centuries as a mortar and as a building material. The early Egyptians used a cement in the construction of the Pyramids, and both the Romans and Carthaginians used a cement that would harden under water in the construction of aqueducts. Some of the Roman structures made out of reinforced concrete are still in good condition (Fig. 96).

The modern cement industry was founded about 1824 by Joseph Aspdin of Leeds, who patented a cement made by burning and pulverizing a mixture of clay and slaked lime. This cement solidified to a material closely resembling, in appearance, the famous Portland (England) building stone; hence, it was called *Portland cement*. The American Society for Testing Materials defines Portland cement as “the

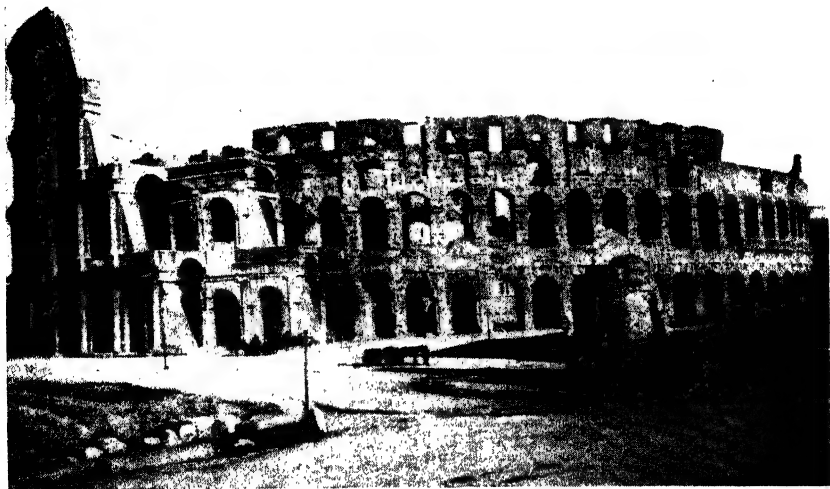


Figure 96. The Colosseum. Its vaulting and piers are of concrete, made with *possuolana*, a volcanic ash calcined by the heat of Mount Vesuvius, and mixed with lime, sand, and water. (*Courtesy of the Portland Cement Association.*)

product obtained by finely pulverizing clinker produced by calcining to incipient fusion an intimate and properly proportioned mixture of argillaceous and calcareous materials, without the addition of anything subsequent to calcination excepting water and calcined or uncalcined gypsum.” If it were necessary to understand this definition to be able to use Portland cement, the building trade would be set back at least fifty years. Portland cement is usually made from a mixture of limestone (calcareous) and clay (argillaceous) although other combinations of similar materials will produce a cement that will come within the scope of the foregoing definition. Some of these combinations are limestone and shale, limestone and cement rock, marl and clay, and limestone and blast-furnace slag.

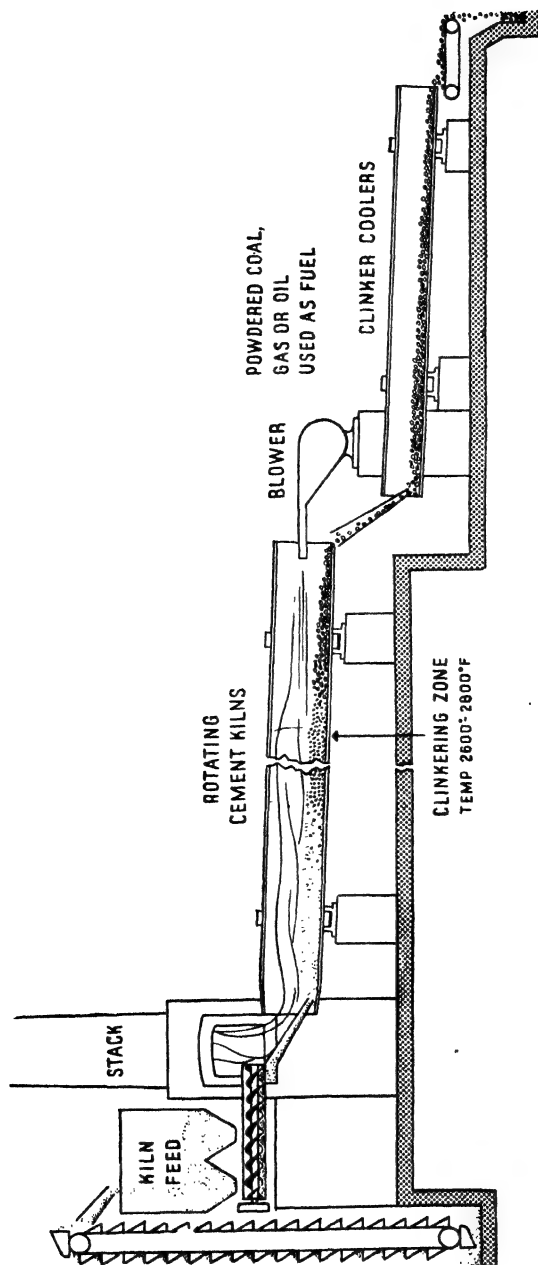


Figure 97. Production of Portland cement. (Courtesy of the Portland Cement Association.)

The raw materials are pulverized and heated to incipient fusion in a rotary kiln that consists of a nearly horizontal tube between 8 and 13 feet in diameter and 100 to 350 feet in length, which rotates at about one revolution per minute. The clay and limestone are added at the higher end of the kiln and travel down it toward a forty-foot flame of natural gas, fuel oil, or powdered coal shooting into the lower end of



Figure 98. Front view of a rotary cement kiln. (Courtesy of the Portland Cement Association.)

the kiln. The time required for the solid material to travel the full distance of the kiln is about two hours, during which time water and carbon dioxide are driven off and the material forms clinkers. The clinkers are air-cooled, 3 per cent gypsum (calcium sulfate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is added, and the mass is pulverized to a palpable powder fine enough to pass through a sieve that will hold water. The resulting product is cement.

The chemistry involved in the hardening of cement in the presence of water is complex and not clearly understood. The hardening takes place in two steps, with the initial hardening associated with the hydrolysis and hydration of some of the oxides in the cement. These reactions take place in about three hours if the cement contains gypsum, which acts as a negative catalyst and lengthens the time before initial hardening, thus permitting easy working of the cement. Other reactions take longer periods of time, and the cement is not "set" until these reactions have gone to completion. There are certain cements high in aluminum oxide content that will set in a day; other cements require times up to a month or more.

Cement itself does not form a desirable product, but when mixed with sand and gravel there is produced the familiar *concrete*. When even greater strength is required, the concrete is reinforced by steel

rods or heavy wire netting. Reinforced concrete as a building material has the double advantage of being very strong when set but plastic before it sets. This permits it to be molded into desirable shapes and to be poured into otherwise inaccessible places. The fact that cement will harden under water has made possible its use in the construction

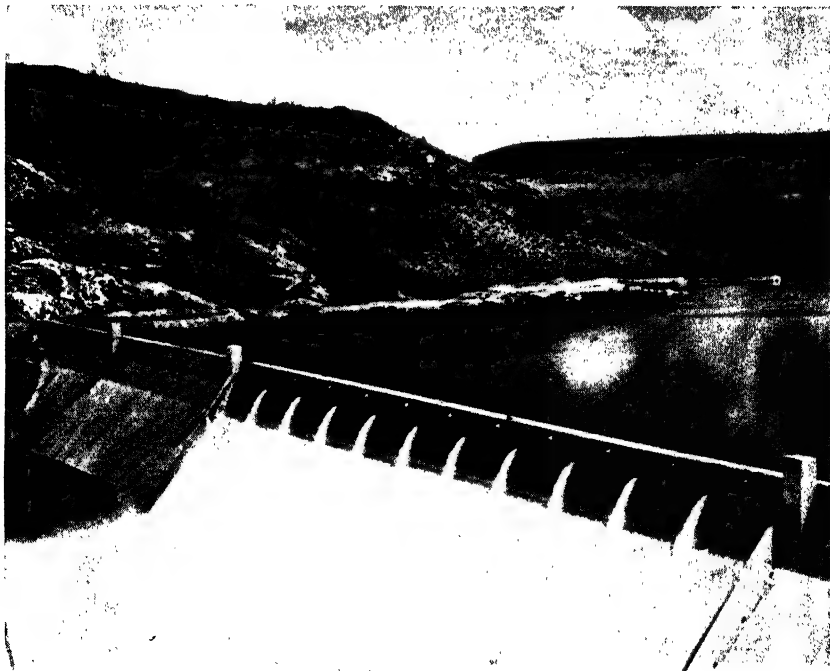


Figure 99. Grand Coulee Dam. The largest concrete dam in the world; 550 feet high and 4173 feet long. (*Courtesy of the Portland Cement Association.*)

of foundations for bridges, piers, and other underwater construction. The modern dam (Fig. 99) as well as the modern skyscraper would be impossible without reinforced concrete.

Nearly all countries have the necessary raw materials for the production of cement. The production of cement in the United States fluctuates widely from year to year; the greatest production was in 1942, with a total of 370 million barrels.

Other Silicates. There occurs in nature a wide variety of complex salts of silicic acid (H_4SiO_4) other than those previously mentioned in

this chapter. These silicates frequently have special uses associated with some particular property. Those used as gems are included in Table 9, Chapter 23, while some others are listed in Table 7.

TABLE 7. Some Common Silicate Minerals*

<i>Name</i>	<i>Formula</i>	<i>Uses</i>
Asbestos	$\text{H}_4\text{Mg}_3\text{Si}_2\text{O}_6$ ($\text{CaMg}_3\text{Si}_4\text{O}_{12}$)	Manufacturing fireproof material
Meerschaum	$\text{H}_4\text{Mg}_2\text{Si}_3\text{O}_{10}$	Tobacco pipes
Mica	$2\text{H}_2\text{KAl}_3\text{Si}_3\text{O}_{12}$	Electrical equipment
Talc (soapstone)	$\text{H}_2\text{Mg}_3\text{Si}_3\text{O}_{12}$	Talcum powder, laboratory table tops, etc.
Zeolite	$\text{H}_4\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{18}$	Water softening

* Silicates used as gems are listed in Table 9, Chapter 23.

EXERCISES

1. *New terms*: ceramic industries, slip, glaze, concrete, frit, glass, bisque, cement, Portland cement.
2. What two properties must a clay possess if it is to be useful in making pottery?
3. Give the chemical names and formulas of the three basic ingredients used in the production of glass.
4. Write equations for the following indicated reactions: (a) the reaction between sodium oxide and silicon dioxide; (b) the reaction between calcium oxide and silicon dioxide; (c) the formation of sodium oxide from sodium carbonate.
5. Why should one expect that pottery making would be an older art than glassmaking?
6. Give two explanations why the earliest examples of glassmaking come from the Nile Valley.
7. Give two reasons why ceramic articles have been made since the dawn of history.
8. What is wrong with defining ordinary commercial glass as "a compound of various silicates together with an excess of silica"?
9. Outline the steps in the production of reinforced concrete from limestone and clay.
10. What is the relationship between (a) kaolin and feldspar; (b) enamel and glass; (c) glaze and glass; (d) cement and Portland stone;

- (c) asbestos and mica; (f) porcelain and chinaware; (g) cement and concrete?
11. What is obsidian? Where would it most likely be found?
 12. Name the two states with the largest deposits of China clay.
 13. Why are red bricks red?
 14. How does Pyrex glass differ from lime glass from the standpoint of both physical properties and chemical composition? Suggest three different uses for Pyrex.
 15. What is the cheapest glue? For what is it used?
 16. What is the difference between plate glass and window glass?
 17. List ten different types or kinds of glass, and give a specific use for each.
 18. Outline the history of glass.
 19. What was the average daily production of bottles and jars in 1947?

COLLATERAL READING

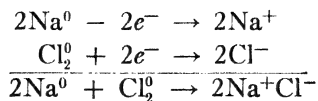
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Electricity in Chemical Processes

IT HAS BEEN emphasized that atoms are essentially electrical in character, the electrons in the outer shells being those portions of the atom which enter into chemical reactions. If electricity is visualized as the passage of a stream of electrons, the question of the possibility of utilizing the transfer of electrons from one atom to another in a chemical reaction as a source of electricity might well be raised. The answer is that it can be and is utilized as a source of electricity; common examples are the lead storage battery and the dry cell.

The opposite type of reaction, the occurrence of a chemical reaction owing to the passage of an electric current, has already been noted in connection with discussions of the decomposition of water by electrolysis. More important examples of this type of reaction will be given in this chapter.

Battery Cells. When chlorine molecules and sodium atoms are brought together, a violent reaction takes place as the sodium atoms lose electrons to chlorine atoms with the resultant formation of sodium chloride (salt). In this reaction the atoms are merely "doing what comes naturally" (Chapter 5); thus the reaction is spontaneous. The transfer of electrons may be depicted as follows:



To utilize this transfer of electrons as a source of electricity it is necessary only to find some way of controlling the reaction and of causing the electrons to pass through a wire on their way from the sodium atoms to the chlorine atoms. With sodium this is not easy, but with less reactive metals it is quite feasible.

The reaction between chlorine and zinc will serve well to illustrate

the operation of a *battery cell* because of the ease with which the reaction occurs and the simplicity of the equipment necessary. Figure 100 represents a simple battery cell that employs chlorine and zinc. Part *A* consists of a carbon rod (electrode) surrounded by a glass tube that is partially submerged in a water solution of zinc chloride, ZnCl_2 (an electrolyte). Part *B* is a zinc rod (electrode) also partly in contact with the solution. When chlorine gas is dissolved in the zinc chloride solution around the carbon rod and a copper wire is connected between the zinc and carbon rods, there is a passage of electrons from the zinc to the carbon. The copper wire serves as a path for the electrons given up by the zinc atoms, Zn^0 , as they become zinc ions, Zn^{++} . At the carbon rod the chlorine atoms that make up the molecules, Cl_2^0 , pick up the electrons and become chloride ions, Cl^- . The zinc chloride solution completes the electrical circuit but does not otherwise enter into the reaction. The flow of electrons is electricity, generated by a chemical reaction; thus is achieved a conversion of chemical energy to electrical energy.

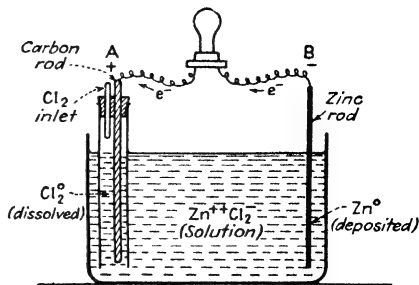
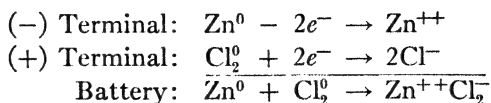


Figure 100. Chlorine-zinc battery cell.

This reaction requires no driving force, for the zinc atoms are losing their electrons so that they may approach the electronic structure of the nearest inert gas, argon. For the same reason chlorine atoms take on electrons to acquire an extranuclear structure like that of the adjacent inert gas.

The chemical and electronic changes in the zinc-chlorine battery cell may be represented as follow:



The current of electricity thus produced by a battery cell is always called a *direct current* because it flows only in one direction—from the negative terminal (pole) to the positive terminal (pole) of the battery.

For a battery to be useful it must combine the ability to perform useful work and have the added features of convenience, low cost, and durability. Because the common storage batteries generally use an aqueous solution of an electrolyte, it is not possible to use active metals such as sodium and potassium, for they react with water. It is also inconvenient to use a gas such as chlorine. The electrodes of a practical battery usually consist of solid elements (both metals and non-metals) and their solid compounds in contact with electrolytes in aqueous solutions.

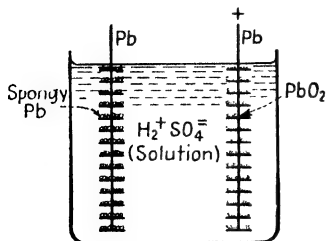
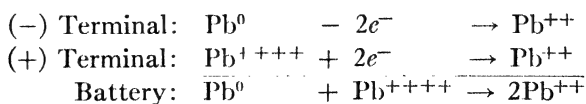


Figure 101. Lead storage battery.

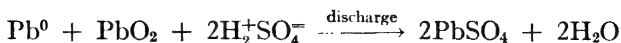
The most widely used battery of this type is the *lead storage battery* used in automobiles. The essential parts of this battery are shown in Fig. 101. The outer case is of hard rubber, and the electrolyte is dilute sulfuric acid solution with a density of 1.250 to 1.275. The negative

terminal consists of a sheet of lead with shelves on it, and these are packed with spongy elemental lead. The positive terminal is of the same construction but contains lead dioxide, PbO_2 . When the battery delivers electricity, the reactions that take place are



This reaction occurs because the lead atoms have a tendency to lose electrons and become Pb^{++} ions and the Pb^{++++} ions have a tendency to gain electrons and become Pb^{++} ions.

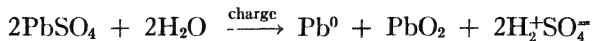
A further chemical reaction takes place owing to the presence of sulfuric acid.



The lead sulfate is insoluble and collects on the lead plates, and the water formed dilutes the acid.

It is obvious that a lead storage battery will last only so long as the supply of lead and lead dioxide is maintained. This is not a serious problem, however, for the reactions that take place during the delivery of current by the battery can be reversed by the imposition of a su-

terior current from an outside source (charging). The lead sulfate dissolves, the water is used up,¹ and spongy lead is regenerated at one electrode and lead dioxide at the other.



The battery is now in its pristine condition and ready for use again. In an automobile this recharging of the battery is done by the generator. A lead storage battery slowly disintegrates mechanically; if this were not so, a battery would last indefinitely.

The extent to which a lead storage battery is discharged can be ascertained simply by measuring the degree to which the sulfuric acid has been diluted by the water formed during the discharge reaction. When the density of the sulfuric acid has dropped to about 1.100, it is time to have the battery recharged.²

The other common battery is the *dry cell* used in flashlights. This battery cell is different from most batteries in that it is made up substantially of solid materials with a minimum of water, and it cannot be conveniently recharged. It is actually not a dry cell but rather a damp cell.

Figure 102 gives a schematic representation of a typical dry cell. The negative terminal consists of the zinc outer case. This case is lined with porous paper that keeps the contents of the cell from coming into direct contact with the zinc. A carbon rod is placed in the center of the cell and constitutes the positive terminal. The rest of the cell is filled with a moist paste of ammonium chloride and manganese di-

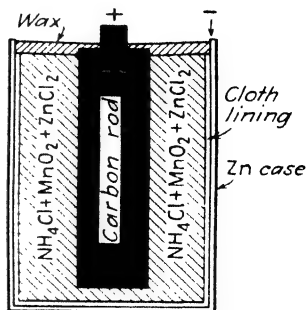


Figure 102. Dry cell.

¹ Not only is the amount of water produced during the discharge of the battery used up, but also some of the water in the original dilute sulfuric acid solution. The extra water is decomposed by electrolysis since the conditions during the charging of the battery are substantially the same as those for the electrolysis of water as noted in the discussion of water and of the preparation of oxygen and hydrogen by electrolysis.

² In Europe the battery that is equivalent to the lead storage battery has as its active materials metallic cadmium and nickel hydroxide, $\text{Ni}(\text{OH})_2$. The electrolyte is a basic solution that permits the use of a steel shell for the battery. Batteries of this type are said to cost about twice as much but to last many years longer than a lead storage battery.

oxide together with a small amount of zinc chloride. The cell is sealed at the top with pitch or wax to prevent evaporation of the water.

The chemistry involved in the operation of the dry cell is complex and will not be represented here by equations.

Electrolysis. The use of electricity to decompose water into oxygen and hydrogen and the chemical reactions caused to take place when a lead storage battery is recharged suggest the possibility of the use of electricity to bring about still other chemical reactions. Not only is this possible, but also electricity is actually one of the chemist's most

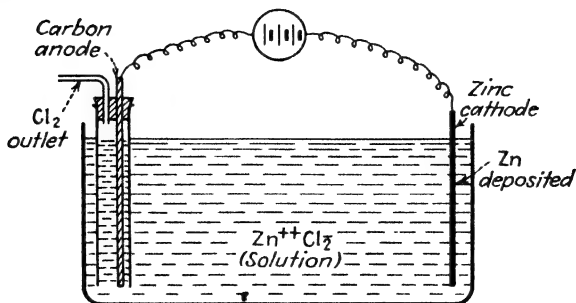


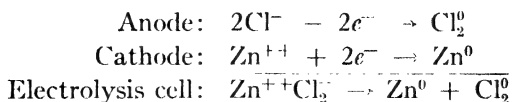
Figure 103. Cell for the electrolysis of zinc chloride.

valuable tools both in the laboratory and in industry. The process of causing a chemical reaction to take place by the passage of an electric current is known as *electrolysis*.

The chemical changes that can be brought about by electricity are many in number and diverse in character. In addition to charging a battery or producing hydrogen and oxygen from water, electrolysis is used commercially to produce sodium hydroxide and a number of metallic and non-metallic elements.

Electrolysis of Zinc Chloride. The apparatus needed for electrolysis is essentially the same as that used in a battery (Fig. 103). For example, if an electrical source stronger than that resulting from the natural tendency of zinc and chlorine to lose and gain electrons is placed in the electrical circuit of a zinc-chlorine battery cell, the battery action is reversed and the zinc chloride electrolyte is decomposed into its elements, chlorine and zinc. The negative chloride ions (anions) will migrate to the positive electrode (anode), there to lose their electrons and become atoms that unite to form molecules of gaseous chlorine. The zinc ions (cations) are positively charged and therefore

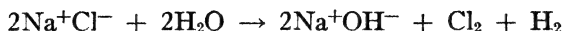
migrate to the negative electrode (cathode) and there acquire two electrons and become zinc atoms, which are deposited on the electrode. The outside source of electricity acts as a "pump" to force the electrons to take this course. The changes that take place are



The electrolysis of a water solution of zinc chloride serves as a good illustration of electrolysis, but the process is not used extensively as a means of producing either zinc or chlorine on a large scale because less expensive methods for their production are available. The cost of electricity prohibits its use in chemistry except in cases where a less expensive means of getting the same results is not possible.

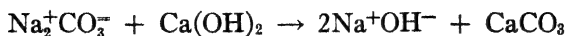
Electrolysis of Aqueous Sodium Chloride Solution. The electrolysis of an aqueous solution of sodium chloride (salt) presents an interesting example of electrolysis wherein two elements and a compound are produced, because the solvent, water, also enters into the reaction. The passage of an electric current through the solution of salt in water results in the expected liberation of chlorine at the anode; but, instead of sodium being formed at the cathode, hydrogen from the water is given off. It is simply a question of the hydrogen ions (H^+) from the water acquiring the available electrons more readily than the sodium ions (Na^+). There are left, in the solution around the cathode, sodium ions from the sodium chloride and hydroxyl ions from the water, and these are the components of the base, *sodium hydroxide* (Na^+OH^-).

The over-all result is the production of chlorine, hydrogen, and sodium hydroxide, all chemicals of industrial importance. The chemical equation is



Different types of cells are used for this electrolysis, that shown in Fig. 104 being one of the more important. Figure 105 illustrates a typical industrial installation of these cells.

Sodium hydroxide is also produced commercially by the reaction between sodium carbonate and calcium hydroxide.



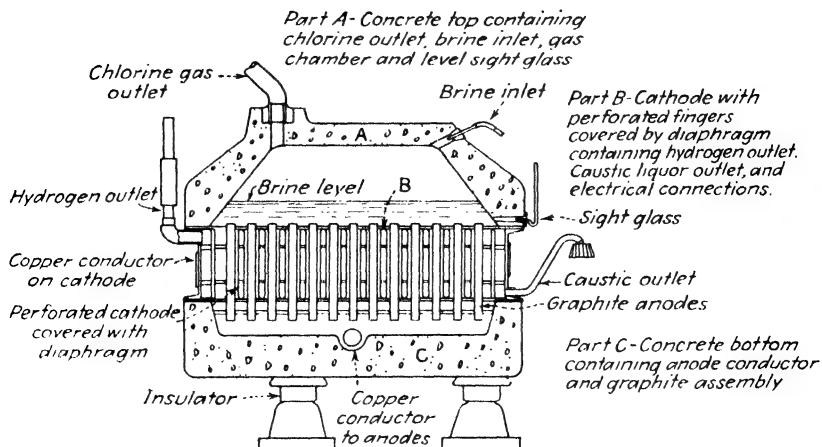


Figure 104. Hooker type S cell for the electrolysis of sodium chloride solution. (Courtesy of the Hooker Electrochemical Company.)

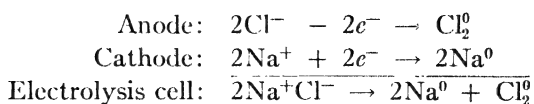


Figure 105. Typical industrial installation of Hooker type S cells for the production of chlorine, hydrogen, and sodium hydroxide. (Courtesy of the Hooker Electrochemical Company.)

The insoluble calcium carbonate is removed by filtration, leaving a water solution from which the sodium hydroxide may be obtained by evaporation of the water. This same procedure is also used to isolate the sodium hydroxide from the solution formed in the electrolytic cell.

Sodium hydroxide (caustic soda) has many uses either in water solution or as a solid in the form of flakes, pellets, or sticks. Over a million tons are used annually in the United States in the manufacture of rayon, pulp and paper, and soap and in the production of a wide variety of chemicals. Sodium hydroxide is also employed in the refining of both vegetable and petroleum oils and in the reclaiming of used rubber.

Electrolysis of Fused Sodium Chloride. For the production of *sodium* there must be no water present, or hydrogen and sodium hydroxide are formed instead of sodium. Sodium is prepared industrially by melting (fusing) salt in a special cell and then electrolyzing the liquid sodium chloride. Chlorine is given off at the anode, and sodium is formed at the cathode.



Sodium is a soft silvery metal that reacts violently with water and rapidly with the oxygen in the air. It is essential to many industries but is rarely brought to the attention of the consuming public. It is utilized in the manufacture of tetraethyl lead (for leaded gasolines—ethyl gasoline), detergents, certain chemicals and pharmaceuticals, and steel. Sodium is also used in the familiar yellow highway lights. It is shipped in 280-pound airtight containers, and it is usually stored in the laboratory under kerosene. Our potential supply of sodium is unlimited.

Other Active Metals. The other active metals, *potassium* and *calcium* in particular, are produced electrolytically in a manner similar to that used for the production of sodium.

Magnesium. Magnesium metal is produced by the electrolysis of magnesium chloride (MgCl_2) obtained directly from the salt brines of Michigan, which contain 3.5 per cent magnesium chloride, or from sea water, which contains only 0.13 per cent magnesium salts. From a percentage standpoint this latter source would not appear to be an especially fruitful one, but even at this low concentration one cubic mile of sea water contains the equivalent of about 6.5 million tons of magnesium.

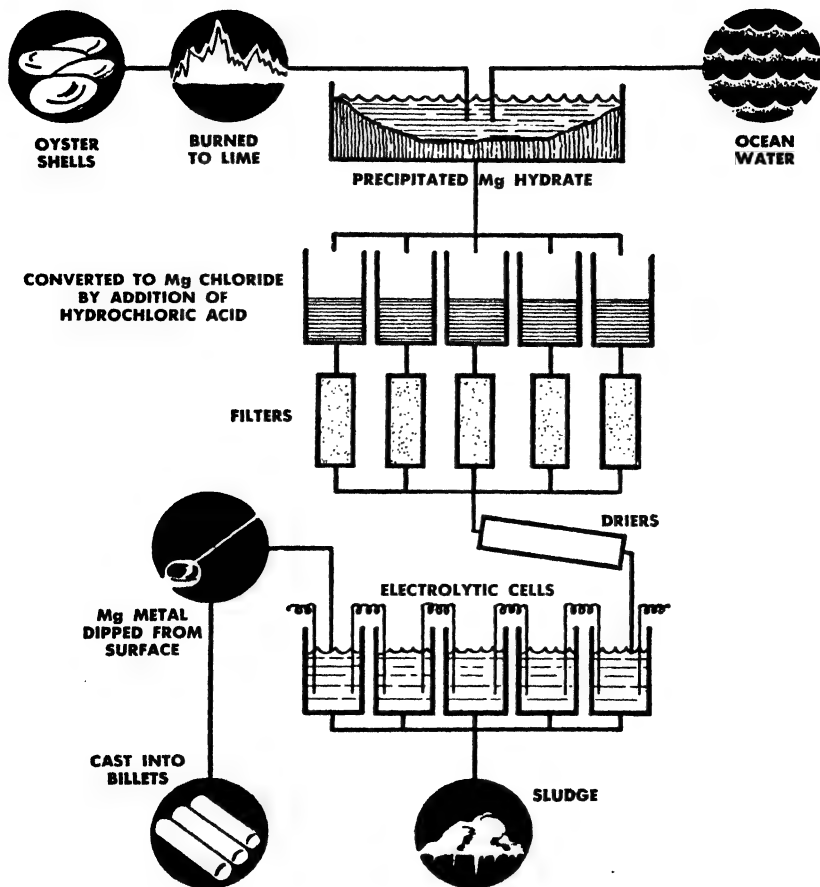
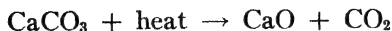
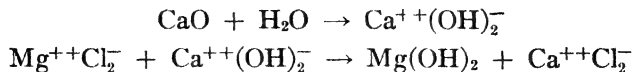


Figure 106. How the Dow Chemical Company produces magnesium metal from sea water. (Courtesy of the Dow Chemical Company.)

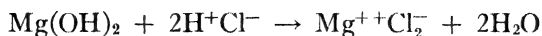
The magnesium chloride is obtained from the salt brine by a simple process of concentration and crystallization. It is not practical to concentrate sea water, however, and hence a chemical method is used (Fig. 106). Oystershell is decomposed to quicklime.



The lime is added to the sea water in sufficient quantity to cause the formation of the insoluble magnesium hydroxide from the magnesium salts present in the sea water.



The magnesium hydroxide is separated by filtration and converted to magnesium chloride by treatment with hydrochloric acid.



The electrolysis of the fused magnesium chloride takes place in cells of steel, the walls of which serve as the cathode. A typical cell (Fig. 107)

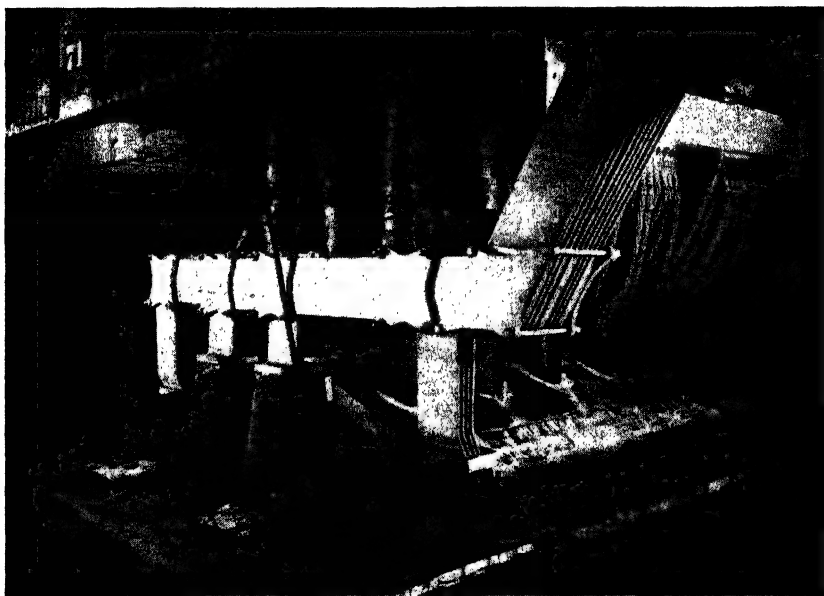


Figure 107. Top of cell used for the electrolytic production of magnesium. (*Courtesy of the Dow Chemical Company.*)

is a steel pot about 11 feet long, 5 feet wide, and 6 feet deep and holds approximately 10 tons of the molten salt at a temperature of 710°C . Carbon rods are the anodes at which the chlorine is liberated. The molten magnesium metal, being lighter than the fused magnesium chloride, floats to the surface and is mechanically removed. The chlorine is burned in natural gas to provide more hydrochloric acid for further treatment of magnesium hydroxide.

During World War II the demand for magnesium became so great that other magnesium compounds could be used economically as raw

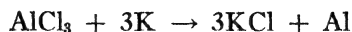
materials, and other methods of production were developed. None of these methods has importance in peacetime economy. During the war period the production of magnesium increased to 73.5 times that of 1939 with a resulting large overproduction of the metal.

Magnesium is the lightest of the common metals; it is only one-fourth as heavy as iron. The single most important use for magnesium is in the production of alloys (Chapter 21), usually with aluminum. They form light, strong alloys used in the production of airplanes, automobiles, streamlined trains, etc. Magnesium is used in the manufacture of signal flares, fire bombs, and other pyrotechnics, in the removal of gases from radio tubes, and in the production and purification of other metals.

About 2 per cent of the earth's crust is magnesium, and it is the third most abundant of the engineering metals (only iron and aluminum are more plentiful). For practical purposes the quantity of raw material available for use in the production of magnesium is unlimited.

Aluminum. The history of aluminum embraces only a little over a hundred years, but in that brief period of time aluminum has changed from a metal more precious than gold and silver to one that has been produced to the extent of more than nine hundred thousand tons in a single year. The reason why aluminum was slow in becoming a metal of wide use and low cost was not the scarcity of its compounds, for it is the most abundant metallic element. Every handful of clay contains aluminum oxide, and aluminum-containing silicates are equally widespread. The basic difficulty resided in the problem of reducing these abundant compounds to their component elements and thus freeing the aluminum.

In 1825 Hans Christian Oersted of Denmark produced the first aluminum by heating aluminum chloride with potassium.



The first bar of aluminum was shown at the Paris Exposition in 1855, and it so intrigued Napoleon III with its potentialities that he commissioned Sainte-Claire Deville to find a way of making the metal cheaply and in large quantities. His degree of success can be measured by the price of aluminum: it was \$545 per pound in 1852 and only \$17 per pound in 1859, by which time a total of two tons had been

produced. This reduction in price was the result of improvements in technique and the substitution of the less expensive sodium for potassium in the reduction reaction. Subsequent improvements in the method of production of sodium so lowered its cost that aluminum could be sold at \$5 per pound.

The problem of the inexpensive production of aluminum was solved on Feb. 23, 1886, by Charles M. Hall and independently, several months later, by a Frenchman, Paul L. T. Hérault. While Hall was still an undergraduate at Oberlin College in Ohio, he set up a laboratory in the woodshed near his father's house and with the help of a sister set out in an endeavor in which noted scientists before him had failed.

Hall rightly guessed that, if a solvent could be found for aluminum oxide (Al_2O_3), the oxide could be electrolyzed to provide aluminum and oxygen. The difficulty was in finding a suitable solvent. Water could not be used, for it would not dissolve the oxide; and when solutions of water-soluble aluminum compounds were electrolyzed, hydrogen instead of aluminum was given off at the cathode. After many failures, Hall discovered that the mineral *cryolite* (Na_3AlF_6) when melted would dissolve aluminum oxide, thus permitting its electrolysis. The cryolite served as the electrolyte, and it was not changed during the electrolysis; the aluminum came from the oxide. The Hall process is the one still used today without any major changes having been made.

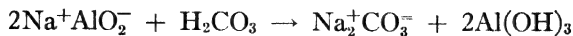
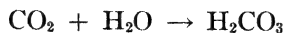
Aluminum oxide is obtained from the ore¹ known as *bauxite*. High-grade bauxite is essentially a pure hydrate of aluminum oxide ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) containing less than 1 per cent of impurities, mainly silicon dioxide (SiO_2), iron oxide (Fe_2O_3), and titanium oxide (TiO_2). The ore is found both on the surface and underground and is mined accordingly (Fig. 108). The principal sources of bauxite are Surinam and Arkansas, although workable deposits are fairly widely distributed over the surface of the earth.

Bauxite is treated with the equivalent of sodium hydroxide in which the aluminum oxide dissolves while most of the impurities do not.



¹ The significance of such terms as ore, mineral, metallurgy, alloy, etc., used in connection with the production of metals will be discussed in Chapter 20.

After filtration, this solution is neutralized with carbon dioxide, and aluminum hydroxide precipitates.



The aluminum hydroxide is calcined to produce aluminum oxide, which is then electrolyzed (Fig. 109). The carbon lining of the cell is the



Figure 108. Strip mining of bauxite in Arkansas. (*Courtesy of the Reynolds Metals Company.*)

cathode at which the aluminum is liberated, and the carbon rods are the anodes where the oxygen is formed. The aluminum settles to the bottom of the cell and is removed periodically. The cell temperature is about $1000^{\circ}\text{C}.$, and the continuous addition of aluminum oxide permits uninterrupted operation.

Two pounds of bauxite, 0.6 pound of carbon electrode, 0.2 pound of electrolyte, and 10 kilowatt-hours of electrical energy are required to produce one pound of aluminum, which sells at about 15 to 20¢ per

pound. This aluminum is 98 to 99 per cent pure. If aluminum of greater purity is desired, the crude aluminum is purified by electrolysis in a

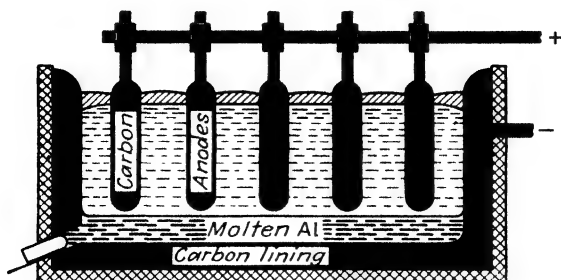


Figure 109. Cell for the electrolytic production of aluminum (Hall process).



Figure 110. A number of electrolytic cells for the production of aluminum by the Hall process. (Courtesy of the Reynolds Metals Company.)

manner similar to the purification of copper, which will be described later in this chapter.

The uses of aluminum are those characteristic of the light metals. Some of these uses were mentioned in connection with magnesium, as

was the close interrelationship of aluminum and magnesium in their alloys. Aluminum is also employed in the form of wires for the transmission of electricity and in the fabrication of many household articles.

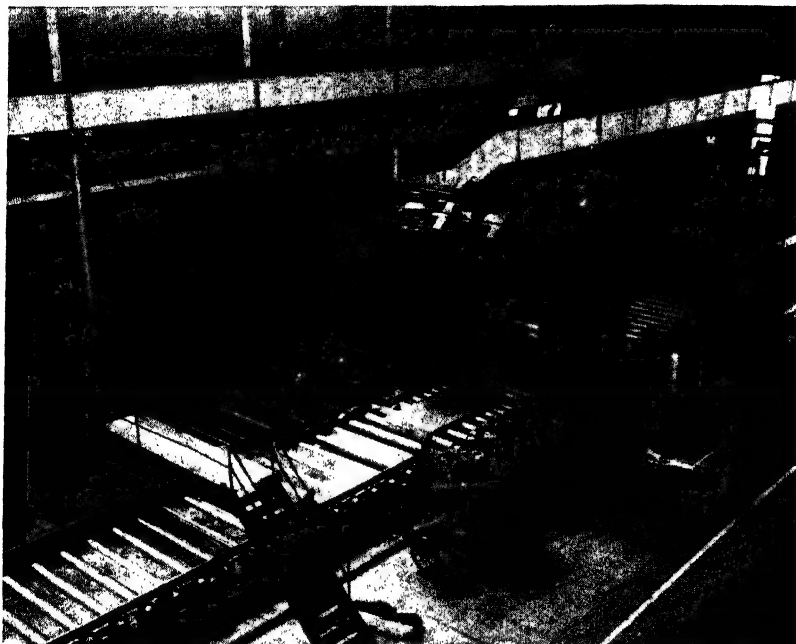


Figure 111. Rolling sheet aluminum. (*Courtesy of the Reynolds Metals Company.*)

In the general discussion of alloys (Chapter 21), other uses of aluminum will be noted.

The United States has sufficient high-grade bauxite to last until 1967 if utilized at the same rate as in 1947.

Purification of Metals by Electrolysis. It has been mentioned that only those metals which cannot be produced by cheaper means are produced by electrolysis. The other methods of production, although having the advantage of low cost, usually do not give a product of as high a purity as does electrolysis. When high purity is desired, it is often necessary to resort to the use of electrolysis, at least as the last step in the process of obtaining the metal from its naturally occurring compounds.

The production of 99.95 per cent pure copper is an example of the

use of electrolytic purification. Copper is made in large quantities and at a low cost by a heating and reduction method (Chapter 20). This product is about 99.5 per cent copper, but for its use as a conductor



Figure 112. Coils of sheet aluminum entering a heat-treating furnace. (*Courtesy of the Reynolds Metals Company.*)

of electricity this 0.5 per cent impurity is highly undesirable because the electrical resistance of the copper is materially increased by the presence of impurities.

The crude copper (99.5 per cent) is cast in the form of slabs weighing about 400 pounds. These slabs are placed in a cell containing a dilute sulfuric acid solution of copper sulfate (CuSO_4) as the electrolyte and a thin sheet of pure copper. The crude copper is the anode of the cell, and the pure copper is the cathode. The passage of an electric current of the correct magnitude will cause the copper atoms at the anode to lose their electrons and dissolve as copper ions (Cu^{++}). At the same time an equal number of copper ions will acquire electrons at the cathode and plate out as pure copper. Eventually all of the copper

from the impure copper anode will be transferred through the solution and deposited on the cathode in the form of pure copper.

The metal impurities in copper are usually zinc, nickel, iron, silver, gold, platinum, and palladium. The first three metals will also go into solution in the form of their ions, but under the conditions of operation employed they will not deposit on the copper cathode. Eventually they accumulate in the solution to an extent that necessitates either purification or rejection of the electrolyte solution. The last four metals do not dissolve but separate mechanically and collect at the bottom of the cell in the form of a sludge (anode sludge).

In Chapter 17 the observation was made that chemical industries were especially adept at utilization of their by-products. The electrolytic refining of copper illustrates the economy of such utilization, for the cost of the electrolytic-purification step is almost entirely paid for by the sale of the precious metals that collect as a by-product in the anode sludge. Over one-fourth of the total production of silver, about one-eighth of the gold, and lesser quantities of platinum and palladium are obtained from this source. Their sale makes possible the production of 99.95 per cent copper at essentially the same cost as the much less desirable 99.5 per cent copper.

A number of other metals are purified in a manner similar to that used for copper. Among these are silver, gold, zinc, and iron; others will be cited in the next chapter.

Electroplating. The ability of certain metals to be deposited on other metals by electrolysis is widely used as a means of coating the more reactive metals such as iron and steel to prevent corrosion and to impart a more attractive appearance. The metals usually employed are silver, gold, platinum, chromium, nickel, and copper, because they can be deposited as a smooth, adherent layer of metal and because they are resistant to chemical attack under atmospheric conditions.

The process of electroplating is essentially the same as for the electrolytic refining of metals. In the silver plating of table cutlery, for example, the object to be plated is made the cathode in an electroplating cell containing a silver salt [potassium argentocyanide, $\text{KAg}(\text{CN})_2$] as the electrolyte and a sheet of pure silver for the anode (Fig. 113). The silver leaves the anode and is deposited on the cathode. Frequently an iron object to be silver-plated is first plated with copper, which adheres well to iron; then the silver is deposited on the copper.

The success of electroplating is dependent upon temperature, current, concentration, nature of the electrolyte, and rate of deposition. If these conditions are not carefully controlled, the metal will flake or crumble. The following electrolytes are used in the plating of the indicated metals: copper, potassium cuprocyanide $[\text{KCu}(\text{CN})_2]$; nickel, nickel ammonium sulfate $[\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2]$; chromium, a mixture of chromic acid (H_2CrO_4) and chromic sulfate $[\text{Cr}_2(\text{SO}_4)_3]$. The chromium plating so conspicuous on the modern automobile is plated on nickel,

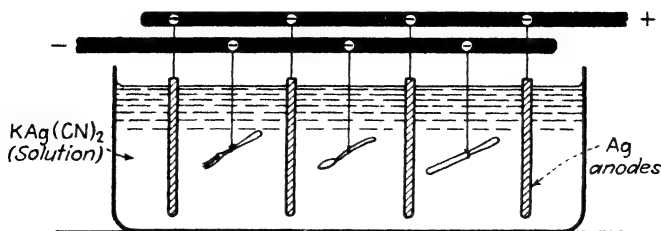


Figure 113. Cell for electroplating cutlery.

which in turn is plated on the original iron or steel. Nickel adheres to iron better than does chromium.

EXERCISES

1. *New terms:* electrode, electrolysis, cathode, electroplating, electrolytic cell, direct current, anode, electrolytic purification, battery cell.
2. Why are so many electrochemical industries located at Niagara Falls?
3. Explain why the reactions in the zinc-chlorine battery are spontaneous ones.
4. Draw a diagram of a lead storage-battery cell, and label the functional parts.
5. What is the fundamental difference between the operation of a battery and an electrolytic cell?
6. Give two reasons why water must be added to a lead storage battery from time to time. Why does this type of battery not last forever?
7. Outline the steps in the production of magnesium from sea water. Write the appropriate chemical equations for each step.
8. Name two light metals widely used in airplane construction.
9. Why is the amount of raw material used for the production of magnesium considered to be unlimited?

10. Outline the history of aluminum.
11. Of what use is anode sludge?
12. What is the relationship between the density of the liquid in a lead storage battery and the degree to which the battery is "charged"? Explain.
13. Why is it necessary to use an outside source of electricity to cause electrolysis to take place?
14. Outline the process used in electroplating silverware. What are some of the factors that govern the success of the operation?
15. Write equations indicating the chemical reactions involved in the charging and discharging of a lead storage battery.
16. Why is a "dry" cell not dry?
17. Name five metals produced by electrolysis.
18. Give five different uses of sodium hydroxide.
19. Where is Surinam?
20. Write equations representing the chemical reactions involved in preparing pure Al_2O_3 from bauxite.
21. If the total production of silver in the United States in 1947 was 33,400,000 ounces, how much silver was recovered as a by-product of the electrolytic refining of copper?

COLLATERAL READING

- ELDER, SCOTT, and KANDA: "Textbook of Chemistry," Harpers & Brothers, New York, 1948, Chapter 18.
- METCALF: "Aluminum from Mine to Sky," Whittlesey House (McGraw-Hill Book Company, Inc.), New York, 1947.
- SCHOCH, FELSING, and WATT: "General Chemistry," McGraw-Hill Book Company, Inc., New York, 1946, Chapters XXI, XXII, and XXIII.

Metals

FROM the beginning of time man has sought health, wealth, and power; and most of the history of the world can be written in these terms. Christopher Columbus was financed by Queen Isabella, not to find a new continent, but to discover a shorter route to the riches of the Far East. Because the New World he found was incredibly rich in various metals, its settlement was hastened by man's search for them, for the possession of metals has been an outward symbol of man's success in the pursuit of wealth and power. The most spectacular evidence of this was the rush to California in 1849, when gold was first discovered there; the foundation for that state's present prosperity was laid at that time. The search for and discovery of metals other than gold has been less spectacular but no less important in the development and westward expansion of the country in the nineteenth century.

Although gold, silver, iron, lead, and copper have long been known and are readily identified by their particular properties of color, weight, metallic luster, etc., they are only a few of the more economically important of the approximately 70 metallic elements.

A metal may be described as an element which forms the positive ion of a simple compound, which has a metallic luster, and which is generally a good conductor of both heat and electricity. There are other less general distinguishing features such as their being solids at room temperature (with but one exception, mercury) and possessing a silvery luster (except gold and copper). Many are heavy, but a few are light. Some metals can be rolled into very thin sheets (*i.e.*, they are *malleable*), while others are brittle; some can be drawn into very fine wire (*i.e.*, they are *ductile*), while others cannot. Metals are usually distinguished one from the other by these differences in physical properties.

There are several terms used in relation to metals in general that need to be defined before specific metals are discussed. A compound of

an element (or the uncombined "free" element) as found in nature is called a *mineral* (Fig. 114). If the mineral is such that a metal or compound can be obtained from it economically, it is an *ore* of that substance; the process of obtaining a metal from its ore is called *metallurgy*. A common step in metallurgy involves heating the ore in air to change the various compounds present into oxides. This process is called *roasting*. Ores are classified as *low-grade* or *high-grade* ores depending upon the relative amounts of desirable material they contain.



Figure 115. Units for the concentration of low-grade copper ore by flotation. (Courtesy of the Kennecott Copper Corp.)

A few metals are found free in nature, but most are in the form of their oxides, sulfides, silicates, carbonates, sulfates, chlorides, and phosphates.

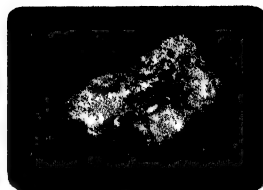
High-grade ores are being utilized at a rate such that much effort is being expended in developing methods of concentrating the more plentiful low-grade ores. One of the most ingenious methods is that of *flotation*. In that process the ore is finely crushed and whipped into a froth with water to which has been added very small amounts of several organic compounds. The ore attaches itself to the air bubbles and rises to the surface, where it is skimmed or floats off. The non-ore material does not stick to the air bubbles and sinks to the bottom of the container. This process is used extensively for the concentration of the sulfide ores of copper (Fig. 115), lead, and zinc although it can also be used for other types of compounds and even for the concentration of free metals such as gold. Ores containing as little as 0.5 per cent to 1.0 per cent of the desired metal are successfully concentrated by flotation.



Malachite
(Tsumeb, Southwest Africa)



Pyrite
(Bingham Canyon, Utah)



**Gold leaf on white
massive quartz**
(El Dorado County, Calif.)



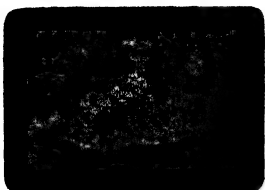
Silver
(Chanarcillo, Chile)



Cinnabar
(Mercur, Utah)



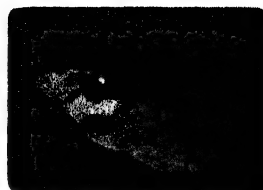
**Hematite, kidney-
type ore**
(Cumberland, England)



Uraninite
(Great Bear Lake,
Northwest Territory)



Calcite
(Joplin, Mo)



Zircon
(Eganville, Ontario)

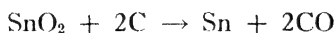
Figure 114 Examples of both common and rare minerals (Courtesy of Ward's Natural Science Establishment)

The metallurgical processes subsequent to concentration vary widely with each metal, and the different methods will be noted in the discussion of the particular metal involved. The important electrolytic refining of metals has already been described (Chapter 19).

Pure metals seldom have properties that make them suitable for a wide variety of uses. The properties of a metal, however, are frequently altered materially by adding a small amount of one or more other metals. The mixture produced by melting together two or more metals is called an *alloy*; nearly all metals as we know them are actually alloys. The subject of alloys will be treated more completely in the next chapter, but certain alloys of the metals mentioned in this chapter will be described here.

Tin. Tin holds the unenviable position in the economy of the United States of being, along with nickel, a widely used metal of which ores have not been found in this country. At present the only sources of the important tin ore, *cassiterite* (*tinestone*), SnO_2 , are the Cornwall deposits in the British Isles and the more extensive deposits in Malay and Bolivia, and these ore beds are large enough to supply the world with tin for only a few more years.

The metallurgy of tin consists in concentrating the low-grade ore (0.5 per cent tin), followed by heating the tin oxide with powdered coal in a furnace. The carbon from the coal reduces the tin oxide to tin, with the simultaneous formation of carbon monoxide.



The molten tin is removed from the bottom of the furnace and cast into blocks. Different methods are used for the purification of the crude tin; electrolysis gives the product of highest purity.

The largest single use of tin is in the manufacture of tin cans. There would be required a vast quantity of tin for the 10 billion tin cans used each year in the United States were it not for the fact that there is only slightly more tin in a tin can than there is horse in horseradish. A tin can consists of steel coated with a very thin layer of tin. When this tin is put on by a hot-dip method, the weight of tin is about 2 per cent of the weight of the can; when the tin is deposited electrolytically, less than 1 per cent by weight of the can is tin. Because of the shortage of tin, other protective coatings for cans have been developed; the most useful ones are silver and various lacquers. Silver can be plated

on steel in a layer so thin that silver plate can compete with the tin plate on a cost basis. The greatest drawback to the use of silver for this purpose is the government's monetary policy, which results in the storing of most of our silver in vaults at West Point, N.Y.

Tin is a component of many alloys such as bronze (Cu, Sn), pewter (Pb, Sn), solder (Pb, Sn), type metal (Pb, Sb, Sn), and bearing metal (Cu, Sb, Sn). "Tin foil" is nearly always either aluminum foil, lead foil, or zinc-coated paper. The compounds of tin are not used exten-



Figure 116. Zinc mine. (Courtesy of The New Jersey Zinc Company.)

sively except as mordants in dyeing (Chapter 28) and in the weighting of silk. They also find limited use as laboratory reagents.

Zinc. In contrast to the lack of tin ore in the United States, there are zinc ores in every state. This wide distribution of ore does not mean, however, that the United States has an unlimited supply. It has been estimated that current known ore deposits will last until about 1970. The United States furnishes one-third of the world's production of zinc.

The two principal ores of zinc are *sphalerite* (*zinc blende*), ZnS , found in the tristate area comprising parts of Missouri, Kansas, and Oklahoma and various silicates of which *calamine* ($2\text{ZnSiO}_3 \cdot \text{H}_2\text{O}$) is of rather widespread occurrence, whereas *willemite* (Zn_2SiO_4) occurs only in the deposits around Franklin, New Jersey (Fig. 116). Idaho also produces considerable quantities of zinc from miscellaneous ores. Zinc ores, especially sphalerite, are frequently associated with ores of other

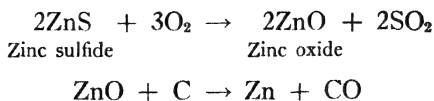
metals such as lead and cadmium. In fact, zinc was produced and used in the form of alloys with other metals long before it was first obtained pure in 1746. One of these alloys, brass (Cu, Zn), was made by heating copper and zinc ores together.

Zinc is produced either by chemical reduction or by an electrolytic process, depending upon various factors such as cost of electricity, purity desired, and nature of the ore. In the chemical process the ore



Figure 117. Retorts which produce spelter zinc from zinc concentrates. (*Courtesy of The Eagle-Picher Sales Co.*)

is concentrated and roasted to change the sulfides and carbonates to oxides, and this material (or the original pulverized ore if it is an oxide ore) is then briquetted with powdered coal. The briquettes are heated in vertical retorts at 1200 to 1300°C. At this temperature the zinc oxide gives up its oxygen to the carbon (coal) with the production of zinc and carbon monoxide; the chemical reactions may be represented by the following equations:



At the temperature of the reaction the freed zinc distills and is collected as liquid zinc in condensers (Fig. 117) from which it is cast into

slabs. This zinc is called *spelter* and contains some cadmium, iron, lead, arsenic, and copper. Spelter is purified by a number of different physical and chemical methods, including distillation (Fig. 118) (zinc boils at $906^{\circ}\text{C}.$).

Zinc is frequently obtained from its sulfide ore by electrolysis. In



Figure 118. Tapping molten zinc from a furnace condenser. (Courtesy of The New Jersey Zinc Company.)

this process the ore is roasted to produce zinc oxide containing some zinc sulfate. The oxide is then dissolved in sulfuric acid and then after suitable purification steps, the zinc sulfate is electrolyzed between lead anodes and aluminum cathodes. The deposited zinc of 99.9 per cent purity is stripped from the aluminum cathode and is ready for use.

Zinc is nearly as heavy as iron and has a brilliant bluish-white luster that rapidly turns to a dull gray upon exposure to air, owing to the formation of a coating of basic zinc carbonate. This thin coating ad-

heres tightly to the metal and prevents further corrosion; consequently, for all practical purposes zinc is considered to be stable in air.

The major use of zinc is as a protective coating on iron and steel. A thin layer of zinc is deposited on especially cleaned iron either by dipping the piece to be coated in molten zinc (it melts at $419^{\circ}\text{C}.$), coating the surface with zinc dust and then melting the zinc, or by electrolysis. The product is called *galvanized iron*. Lesser amounts of zinc are used to produce alloys [brass and German silver (Cu , Zn , Ni)] and in the manufacture of dry-cell batteries, sinks, gutters, cornices, weather strips, lithographers' sheets, engravers' photo plates, etc. Many automobile parts such as fuel pumps, handles, radiator grills, and light fixtures are zinc alloys. About one-fourth of the zinc produced is used in the manufacture of brass and other alloys used for die casting. During World War II a zinc alloy was used for the production of pennies, but they were hardly worth the price.

Only a few compounds of zinc are important. The use of zinc oxide and zinc sulfide as pigments in paint is mentioned in Chapter 32. Zinc oxide is also used as a "filler" in automobile tires, in face powders, and in the manufacture of enamels and glass. The oxide has some therapeutic value and is used in ointments. Zinc chloride, ZnCl_2 , is used as a wood preservative.

Lead. Lead is one of the metals that has the distinction of mention in the Old Testament as having been found among Solomon's treasures. It has been found in ancient Egyptian ruins, and the Romans used lead water pipes. Lead has been used for roofs for centuries; some are still in existence after nearly 1500 years (Fig. 1). Glass in the windows of the great cathedrals of the Middle Ages was set in lead.

Lead occurs free in nature to a small extent, but the most important ore is *galena*, PbS , found in Missouri, Oklahoma, and Idaho as well as in many other parts of the world. The United States imports lead from Mexico, Canada, and Peru to supplement the domestic supply. It has been estimated that the supply of reasonably high-grade ore in the United States will last until about 1960.

The metallurgy of lead is rather simple, but the chemical reactions involved are many and complex. The ore is concentrated and then roasted to change the galena to a mixture of lead monoxide, PbO , and lead sulfate, PbSO_4 , along with some unchanged lead sulfide. The impurities, including copper, iron, zinc, arsenic and bismuth sul-

fides, are changed into the corresponding oxides. To this mixture are added limestone, iron ore, and carbon (coke), and the material is heated in a furnace while a blast of air is forced through the mixture. Many reactions take place, but the production of lead is the ultimate result. The molten lead is drained from the furnace and purified by one of several different methods.

Lead is purified not only because some of the metallic impurities are valuable but also because even very small amounts of certain metals dissolved in lead make it unsuitable for many of its uses. The *Parkes process* consists in adding zinc and melting the resulting mixture. The dissolved copper, silver, and gold are more soluble in zinc and are therefore extracted from the lead. The zinc is removed, and the valuable metals are recovered from it. The *Betts process* is very similar to the electrolytic refining of copper (Chapter 19) and produces a pure lead. Just as in the case of electrolytic refining of copper, there is formed an anode sludge rich in gold and silver that helps to pay the costs of operation.

Pure lead is a soft, bluish-gray metal that is malleable but not very ductile. It forms an oxide readily upon contact with air, but this provides a protective coating that prevents further action. Lead is one of the heaviest of the common metals (density = 11.34); it melts at 327.5°C. and boils at 1600°C.

The largest use of lead is in the manufacture of lead storage-battery plates, while lesser amounts are employed in the production of lead pipes, electrical-cable coverings, rifle bullets, linings for sulfuric acid tanks, etc. About 74 per cent of the lead is used for these purposes; the remainder is used to make chemicals such as tetraethyl lead, insecticides, and compounds used as pigments in paints (Chapter 32). The use of lead in alloys has been mentioned in the discussion of both tin and zinc.

Lead compounds are highly poisonous, and their effect is cumulative; small quantities taken over a long period of time are nearly as dangerous as the same amount taken all at once. Lead poisoning is not uncommon, because of the extensive use of lead compounds in gasoline and paint; due caution should be exercised in handling these materials.

Nickel. Nickel was first produced (1751) from a German ore that looked like a copper ore but that would not yield any copper. The Germans, in their annoyance, named the ore *Kupfernickel* (Old Nick's

copper), from which the name nickel is derived. Nickel has been found alloyed with iron in meteorites, but its commercial source is the ore *pyrrhotite*, a mixture of the sulfides of iron, nickel, and copper. About 85 to 90 per cent of the world's supply of nickel comes from the pyrrhotite ore deposits at Sudbury, Ont.

Owing to the complexity of the ore, the metallurgy of nickel is diffi-



Figure 119. Drilling nickel ore 1200 feet underground. (Courtesy of *The International Nickel Co.*)

cult and expensive. In one process the final step is the reaction of carbon monoxide with nickel to form nickel carbonyl, $\text{Ni}(\text{CO})_4$, which is subsequently decomposed to yield pure nickel. In another process, substantially pure nickel is deposited by electrolysis, and an appreciable amount of platinum is produced as a by-product. Approximately 40 tons of ore is required to produce one ton of nickel.

Nickel is a silver-white metal that is hard, malleable, and magnetic. It is resistant to atmospheric corrosion and is used to some extent as a plating material. In a finely divided state, nickel is used as a catalyst for a number of chemical reactions.

Nickel is a component of many alloys, some of which have been mentioned (German silver) and others of which will be noted in the

next chapter. Pure nickel as well as its copper alloy, cupronickel, has been used for coins since 1850. The Canadian 5¢ piece is pure nickel, while the United States 5¢ piece is an alloy containing 25 per cent nickel and 75 per cent copper, as do the Luxembourg 1-franc pieces and the French 10-franc pieces. During World War II the nickel of a 5¢ piece was replaced by silver (Ag 35 per cent, Cu 56 per cent, Mn 9

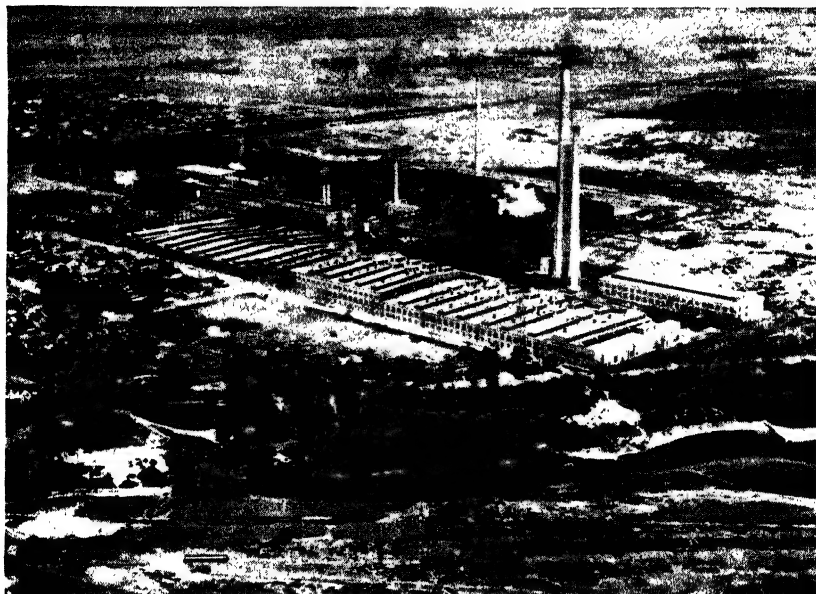


Figure 120. Aerial view of The International Nickel Company plant at Port Colborne, Ontario. (*Courtesy of The International Nickel Co.*)

per cent). Part of the silver in the coins of India has been replaced by pure nickel, which is well suited for use in coinage because of its attractive appearance, resistance to wear, and difficulty of counterfeiting.

The compounds of nickel are not of great importance.

Copper. Although the history of copper dates back at least five thousand years to early Egyptian statuettes made of this metal, there is no reason to believe that copper was unknown before this time. The reasons for the early use of copper were the wide distribution of its ores, the ease with which the copper could be obtained from its ores, and the fact that copper also occurs free in nature, especially in the Lake Superior region of the United States. However, ores containing

free copper account for only a small percentage of the approximately one million tons of copper produced each year in the United States.

Paul Revere (Fig. 91, Chapter 18) of Revolutionary War fame deserves an even higher place among the heroes of the United States than he achieved by his midnight ride because of his discovery of the secret process for making copper malleable, a secret known only to the British. Paul Revere was not only a horseman of renown but also an artisan in gold and silver and the founder of the important malleable-copper industry.



Figure 121. An open-pit copper mine. Bingham Canyon, Utah.

Many different ores are used in the metallurgy of copper, but the following three are the most important: *chalcopyrite* (CuFeS_2), *chalcocite* (Cu_2S), and *bornite* (Cu_5FeS_4). About 70 per cent of the copper ores in the United States are sulfides. The principal producing areas of the United States are in Arizona, Montana, Utah, Nevada, and Michigan; of these, Arizona produces about two-fifths and Montana one-fifth of the total.

The metallurgy of copper varies with the nature of the ore, but in general there are four steps: (1) *concentration*; (2) formation of *copper matte*; (3) production of *blister copper*; (4) *electrolytic refining*. The first and last steps have been described in connection with flotation and under the heading of Purification of Metals by Electrolysis in Chapter 19.

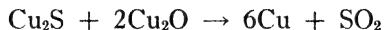
The copper matte is made by a partial roasting of the concentrated ore in a furnace. This roasting causes a partial conversion of the sulfides

and complete conversion of the carbonates to oxides. Limestone or similar material is added, and silicates are formed from the silica and iron compounds in the ore when they react with the calcium oxide from the limestone. This mixture of silicates, called *slag*, is lighter than the molten mixture of copper and iron sulfides (*copper matte*) and can easily be removed.



Figure 122. Electrolytic copper-refining plant. (Courtesy of the Anaconda Copper Mining Company.)

The copper matte is heated in a special type of furnace through which air is blown to change the iron sulfide to the oxide and some of the copper sulfide to its oxide. More sand is added, and the iron oxide forms a slag of iron silicate. The copper oxide (Cu_2O) reacts with the copper sulfide (Cu_2S) to form copper and sulfur dioxide.



This copper is called *blister copper* and is the material used for the production of pure copper by electrolysis (Fig. 122).

All of the sulfur in the sulfides of the original ore eventually become sulfur dioxide, and this constitutes an important source of sulfur dioxide (Chapter 22).

Copper is distinguished by being one of the two colored metals. It has a reddish "coppery" color and is soft, malleable, ductile, and a good conductor of heat and electricity. Copper melts at 1083°C. and has a density of 8.95.

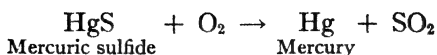
About 80 per cent of the copper is used for copper products and 20 per cent for alloys. The most important of the copper products are wire and bus bars for the transmission of electricity. It is also used for vats, stills, etc., in the alcoholic-beverage industry (Chapter 29). An appreciable amount of copper is used by the building trade in the form of sheets and strips. The alloys of copper, of which there are more than a thousand, that have not been mentioned previously will be considered in Chapter 21.

Copper sulfate, CuSO_4 , is perhaps the most important compound of copper; its uses have been given in Chapter 16.

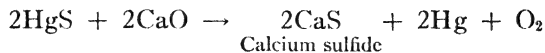
Mercury. Mercury, or *quicksilver*, was known at least as early as 1600 B.C., and during the time of Buddha it was taken internally for the relief of constipation. Owing to the fact that mercury is heavy, it was often used by alchemists in their search for an easy way to make gold. During the thirteenth century it was used extensively for the treatment of cancer, gout, scabies, and leprosy, and in the fifteenth century it was used for the treatment of syphilis. The early use of mercury resulted from the fact that its metallurgy is relatively simple.

The chief ore of mercury is *cinnabar*, HgS , which is mined in appreciable quantities in Spain, Italy, and the United States. The principal producing areas of the United States are California, Oregon, and Texas. In California and Oregon there are a few deposits of free, or native, mercury, and this may be obtained from the surrounding rock by simple distillation. Mercury boils at 357°C. and solidifies at -39°C . The known reserves of high-grade cinnabar and mercury ores in the United States are estimated to be sufficient to last until about 1950; at present the United States imports about 50 per cent of its supply of mercury.

Two methods are used in the metallurgy of cinnabar. One method consists in heating the cinnabar in air.



At the temperature of the reaction the mercury distills off and is condensed as liquid mercury. The other method comprises the heating of cinnabar with calcium oxide.



The mercury distills away from the solid calcium sulfide.

Mercury is purified by filtering it through chamois skin to remove the gross impurities; then it is dropped through a solution of mercurous nitrate, HgNO_3 , and nitric acid in water. The remaining impurities dissolve in this solution, leaving pure mercury.

Mercury is unique in being the only liquid metal, although there are others that melt at temperatures only slightly higher than normal room temperature. Mercury has a silvery color and is very heavy (its density at 0°C . is 13.6). The fact that mercury is a heavy liquid with a low vapor pressure and that most gases are insoluble in it recommends it for use as a confining liquid for the collection and analysis of gases. Mercury is used extensively in thermometers, barometers, and other scientific instruments. It is also used in mercury-vapor lamps and in fluorescent lamps. Because of the high boiling point and stability of mercury it is used as a heat-exchange medium (Chapter 12).

Liquid mercury will dissolve most metals with the exception of iron, nickel, and platinum; the alloys thus formed are called *amalgams*. Amalgams are used in the metallurgy of silver and gold (*vide infra*). An amalgam with silver and tin is used for fillings in teeth.

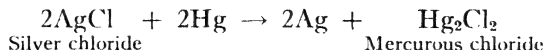
Numerous compounds of mercury are poisonous, but in spite of this they have found use in medicine. *Calomel*, Hg_2Cl_2 , has been used in the treatment of cirrhosis and as a purgative and diuretic. Its use is not without danger, for calomel is easily changed by air and sunlight into *corrosive sublimate*, HgCl_2 , an extremely poisonous compound used as a germicide. Other salts of mercury are of lesser importance; some important organic mercury compounds are mentioned in Chapter 30.

Silver. Silver has been used for jewelry and ornaments since prehistoric times, and it was used for the manufacture of coins in India and Egypt long before the Christian Era. Although silver has been prized as a precious metal and at one time was more costly than gold (Chapter 1), the discovery of large quantities of silver in the Western Hemisphere has made silver a relatively inexpensive metal costing

about one-fiftieth as much as gold. At present Mexico produces about one-third of the world's supply of silver, the United States being the second largest source. Much of the silver obtained in the United States is a by-product of the refining of copper, lead, and zinc.

Free, or native, silver constitutes one of the important sources of the metal as do its naturally occurring alloys with gold, mercury, and other metals. The two compounds of silver that occur in the principal ores are Ag_2S in *argentite*, or silver glance, and AgCl in *cerargyrite*, or horn silver. The sulfide ores commonly occur in small amounts along with the sulfides of the other metals, and the silver is usually a by-product of the metallurgy of these other metals.

Free silver may be separated from the surrounding material either by forming a silver amalgam with mercury or by dissolving the silver in a dilute solution of cyanide. In the *amalgamation process* the silver is recovered by distilling away the mercury. In the *cyanide process* the silver is precipitated by adding metallic zinc or aluminum to the solution. These metals replace the silver in the solution, thus causing the silver to precipitate. Silver may be obtained from cerargyrite by treatment of the ore with mercury, but in this case the amalgamation is preceded by a chemical reaction.



Sulfide ores of silver are subjected to various treatments all of which are designed to get the silver into a water solution in the form of a salt. The silver is then precipitated by the addition of a more active metal. For example, the different sulfides in a typical ore are all converted to sulfates by roasting, and the silver sulfate is leached out of the mixture by the water. The silver is then precipitated by the addition of copper.



In another process silver chloride (AgCl) is formed and dissolved in a sodium cyanide (NaCN) or potassium cyanide (KCN) solution from which the silver is precipitated by the addition of finely divided zinc. The crude silver produced by these processes usually contains gold, copper, and other metals as impurities. Pure silver is obtained by several processes, including electrolysis.

Silver is a heavy white metal that is harder than gold, softer than

copper, and extremely malleable and ductile. Of all the metals, silver is the best conductor of heat and electricity. It is stable toward atmospheric corrosion, with the one exception that it will tarnish in the presence of an atmosphere containing hydrogen sulfide, H_2S , and sulfur-containing food materials. Black silver sulfide is formed. This tarnish can be easily removed by heating the cutlery with soda solution in an aluminum pan. The chemical reactions are electrochemical in nature and complex.

The use of silver as a coating for less stable metals has been mentioned previously in the discussion of electroplating (Chapter 19). Mirrors are made by depositing silver on glass by chemical means. The addition of about 10 per cent of copper to silver produces an alloy that is much harder than pure silver; this type of alloy is widely used for both jewelry and coins. *Sterling silver* contains 92.5 per cent silver and is used for silverware and in British coins. The United States silver coins contain 90 per cent silver, and most silver jewelry contains about 80 per cent silver. The term "sterling silver" is sometimes used rather loosely in referring to the silver content of jewelry.

When there is a scarcity of tin and copper, silver is used to replace them for various uses such as components of solder (2.5 per cent silver and 97.5 per cent lead) and bus bars to conduct large amounts of electricity through short distances, as in electrolytic cells. More silver would be used for industrial purposes if its price were not artificially maintained at a high level by government purchases.

Silver nitrate, AgNO_3 , is the compound of silver known as *lunar caustic* and used in medicine to cauterize wounds and to remove warts and in the manufacture of indelible inks. Silver bromide, AgBr , and, to a lesser extent, silver chloride are very important because of their use in photography.

*Black-and-white Photography.*¹ Black-and-white photography is dependent upon the fact that light affects silver bromide in such a way that by subsequent treatment the silver bromide can be decomposed to silver. The amount of silver formed is dependent upon the quantity of light to which the silver bromide has been exposed. The nature of the chemical reactions involved can best be indicated in terms of the five primary steps in the production of a photographic print (Fig. 123).

¹ The chemistry of color photography involves organic chemistry and is too complicated for inclusion in this book.

1. *Production of the film or plate.* A thin layer of gelatin containing a dispersion of colloidal silver bromide is placed on a transparent film or glass plate. After drying, the film or plate is ready for use. The film or plate must at all times be kept in the dark, or the silver bromide will turn to silver prematurely.

2. *Exposure.* A camera is simply a convenient apparatus that per-

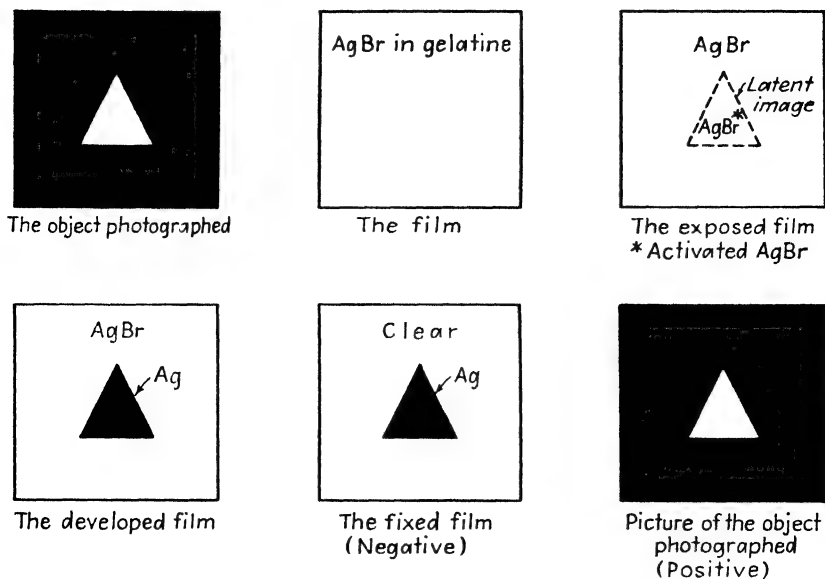


Figure 123. Steps in the production of a photograph.

mits one to expose the film to light reflected from the object being photographed. The object has light and dark areas, which reflect light of different intensities. These different intensities of light in turn affect the silver bromide differently to produce on the film a *latent image* composed of activated silver bromide. At this point the film appears to be unchanged, for the changes brought about by a small amount of light acting on silver bromide are too subtle for the human eye to distinguish.

3. *Developing.* The latent image is developed into a real image by bringing the exposed film into contact with a solution of certain organic compounds (*developers*) that are mild reducing agents. The more activated silver bromide reacts more rapidly than the less activated

silver bromide, with a resulting difference in the amount of silver deposited. The largest amount of silver is deposited in the areas that were white in the object photographed, because white reflects the most light and consequently activates the most silver bromide. The latent image has been developed, but it is still necessary to remove the unchanged silver bromide lest it also be changed to silver in the prolonged presence of light. This would result in a uniform coating of silver over the film and hence no picture.



Figure 124. Negative. (Courtesy of the Eastman Kodak Company.)

4. *Fixing*. In the fixing bath, the silver bromide remaining on the film is dissolved by a chemical reaction with sodium thiosulfate (*hypo*), $\text{Na}_2\text{S}_2\text{O}_3$. The film may now be brought into the light. The image on the film is the reverse of the object photographed because dark silver is deposited where light from the light portions of the object photographed hits the silver bromide. Because of this reversal, the developed and fixed film is said to be a *negative* (Fig. 124).

5. *Printing*. To obtain a *positive* (Fig. 125) all that is necessary is to shine a light through the negative onto paper containing a gelatin film of silver bromide. The same process of developing and fixing as was used for the negative is then followed. In this case no light passes through the silver on the negative; thus the silver bromide is not activated in those areas, and on subsequent developing and fixing no silver will be deposited. If the print is made on white paper, there appears a white area, which corresponds to a white area on the object photographed. Clear areas on the negative permit the passage of light and the subsequent precipitation of silver on the print at those areas and a black design corresponding to the dark portion of the original image. Various shades of gray result from intermediate light intensities and less dense deposits of silver on the negative.

The extent of the use of silver in photography is indicated by the

fact that the Eastman Kodak Company alone used about 300,000 pounds of silver annually (Fig. 126).

Gold. Gold was probably the first metal used by man. It is mentioned in the Old Testament and in Homer's "Iliad" and "Odyssey." The reason for the early use of gold was that it was widely distributed and its color made it easy to find. In these early days various methods were used to obtain gold, and the fact that some of these methods were indeed crude is indicated by the following quotation:

Herodotus reported that in Greece gold was recovered from gold-bearing, lake-shore deposits by dragging pitch-daubed feathers in the wet sand. The further comment that the work was done by virgins is of social rather than scientific interest. The Golden Fleece that Jason stole was probably the sheepskins used to line the bottoms of gold sluices.¹

It has been said that gold is where you find it, but it should also be added that one is more likely to find gold in some places than in others. The ocean is a fruitful source because it contains enough gold to furnish every man, woman, and child in the world \$15,000,000 worth. Unfortunately at present it costs more to recover the gold from the ocean than the gold is worth. The soil in one's back yard contains more gold than an equivalent amount of sea water but is equally difficult to extract. From this it is plain that there is no shortage of gold; it is just too evenly distributed to be recovered economically.

Gold is mined in many localities, but California, Alaska, South Dakota, and Colorado are the most important producing areas. Nearly all of the gold occurs as free or native gold. The only compound of gold of importance is *sylvanite*, $(\text{AuAg})\text{Te}_2$, mined in Colorado. Native gold is found in *vein deposits* along with very large quantities of other ma-



Figure 125. Positive print. (Courtesy of the Eastman Kodak Company.)

¹ Arthur F. Taggart, *American Scientist*, **35**, 85 (1947).



Figure 126. Silver bars used to make silver bromide for photography. There is one ton of silver on the truck. (Courtesy of the Eastman Kodak Company.)



Figure 127. A gold mine in the Rocky Mountains.

terials, usually quartz. Ore of this type may contain only a fraction of an ounce of gold per ton of ore. Gold is obtained to a much lesser extent from *alluvial deposits* in gravels laid down by streams; this was the type of gold found in California during the gold-rush days.

The metallurgy of gold is much like that of silver. The gold-containing gravel or pulverized ore is passed over mercury in which the gold dissolves, or the pulverized ore is left in contact with a cyanide solution for several weeks. The gold dissolves in the solution and is recovered by adding zinc or by electrolysis. The amalgamation process is ordinarily used for the richer ores, while the cyanide process is used on the very poor ones. Gold is purified by electrolysis as well as by several other methods.

Gold has a characteristic yellow or "gold" color, and it is the most malleable of the metals—it can be hammered so thin that 300,000 sheets of gold are required to make a stack an inch in height. Gold is also very ductile and is about 70 per cent as good a conductor of heat and electricity as silver. It is a soft metal and very unreactive.

The color of gold coupled with its weight, scarcity, and high price (\$35 per ounce) makes it suitable for use as jewelry and for coins. Gold itself is too soft for these uses; but, like silver, if a small amount of copper is added to it, the resultant alloy is much harder. The British gold coins contain 92.5 per cent gold, while the United States gold coins contain 90 per cent gold. In each case the remainder of the alloy is copper.

The purity of gold used for jewelry is measured in *carats*. Twenty-four-carat gold is pure gold; 18-carat gold contains 75 per cent gold, 10 to 20 per cent silver, and 5 to 15 per cent copper. Even 18-carat gold is too soft to wear well, and therefore the common gold of jewelry is 14 carat, containing 58 per cent gold and varying amounts of silver and copper. Twelve-carat gold is 50 per cent gold, while the remainder consists of other metals. White gold and the different colored golds contain varying amounts of different metals such as silver, copper, platinum, palladium, and cadmium.

Gold plating is done by electrolytic deposition, and *rolled gold* is made by applying thin sheets of gold to a metal and rolling it down. A *gold-filled* object is composed of an alloy of gold containing very little gold; the lowest recognized standard is 9-carat gold.

The compounds of gold are of little importance, and gold itself has

essentially no industrial importance other than as a monetary standard. The price of gold is determined, not by the laws of supply and demand or the inherent worth of the metal, but rather by civil law.

The Platinum Metals. The platinum metals are ruthenium, rhodium, palladium, osmium, iridium, and platinum. Of these metals only platinum, palladium, and iridium are of much importance.

The platinum metals occur free in nature, but they are not plentiful. They are also extremely unreactive. Because of these properties they were generally either overlooked or considered as undesirable impurities in more valuable metals. It was not until the eighteenth century that platinum was adequately characterized although it was first observed in Mexican silver in the sixteenth century. For a time the importation of platinum into Spain and Portugal was prohibited because counterfeiters coated it with a thin layer of gold. In 1828 Russia actually used platinum as a coinage metal. At present the United States utilizes about 375,000 ounces of platinum metals yearly.

Platinum and the other platinum metals occur together as small grains. The ore is found on all the continents; Russia, Canada, and South Africa are the leading producers. The metallurgy of these metals is very complex and will not be discussed here. It has already been mentioned that platinum and palladium are by-products of the refining of nickel, copper, and gold, and this constitutes an important source.

The platinum metals have high boiling and melting points, and they are harder than iron. Platinum and palladium are malleable and ductile. All of these metals are silver white, with the exception of ruthenium and osmium, which are iron gray. They are all very unreactive, and consequently they do not tarnish or corrode in air.

Platinum is both the most plentiful and the most valuable of the platinum metals. About 50 per cent of the platinum produced is employed for jewelry, a use for which it is particularly suited because of its pleasing appearance and high cost. Most platinum jewelry contains 10 per cent iridium to form a hard alloy that wears better than pure platinum, which is relatively soft. The addition of iridium does not constitute a cheapening of the platinum, however, for iridium costs several times as much as platinum.

An appreciable amount of platinum is used in dentistry for braces, etc., and in the electrical industry. It is used by the chemical industry

as a catalyst and for the fabrication of heat- and chemical-resistant equipment. Platinum would be utilized much more extensively by industry if the manufacturers of jewelry did not require so much and maintain such a high price. It is unfortunate that so valuable a metal is used in an essentially non-productive industry at the expense of its use along more productive lines.

During World War II the use of platinum for jewelry was prohibited, and *palladium*, the next most abundant of the platinum metals, was used as a substitute. It is as resistant as gold to atmospheric corrosion, and it is harder than platinum. The use of palladium in jewelry has continued, and it is also used in dentistry and in the electrical industry.

The principal use of *iridium* is to harden platinum, while a small amount is used by the electrical industries. The standard meter bar (Chapter 8) is a platinum-iridium alloy. This alloy was used because it is stable and has a low coefficient of expansion. An iridium alloy is also employed for the tips of some ink pens.

It should be recognized that the United States supply of easily workable ores of many of the metals mentioned in this chapter will not last more than a few years longer if they continue to be used at the current rate. Before many years this country will become a "have-not" nation. What can be done about it? There are several answers. One of the obvious answers is to find more ore deposits, and more will probably be discovered. When the metals become scarcer, the price will go up and it will then be feasible to work the known deposits of low-grade ores. It is also possible to substitute alloys of the light metals for some of these scarce metals and to substitute plastics for the light metals. The United States will have to purchase more and more of both metals and ores from other countries. The outlook is not bright; neither is it black so far as the present generations are concerned.

EXERCISES

1. *New terms:* metal, mineral, roasting, flotation, blister copper, cyanide process, latent image, carat, gold-filled, malleable, ore, low-grade ore, spelter, copper matte, sterling silver, negative, gold plating, free (native) metal, ductile, metallurgy, high-grade ore, galvanized iron, slag, amalgam, developer, positive, rolled gold, alloy.

2. Account for the fact that certain metals have been in use by man for at least as far back as recorded history.
3. List five ores of which the known high-grade deposits in the United States may be exhausted within twenty-five years.
4. Why was the development of the flotation process in metallurgy of distinct benefit to the United States?
5. When a metal of high purity is desired, what method of purification is most frequently used?
6. Name two common metals the ores of which are not mined in the United States.
7. Name two metals frequently obtained as by-products in the metallurgy of less costly metals.
8. Name three coinage metals.
9. What metal is commonly used to harden both gold and silver?
10. Why is it dangerous to use calomel that has been stored in a clear bottle?
11. Why are gold and platinum especially suitable for use in dentistry?
12. Relate the occurrence of certain metals in the free or uncombined state in nature to their chemical reactivity.
13. Why is a tin can not a tin can?
14. Write equations indicating the chemical reactions involved in the metallurgy of (a) tin; (b) mercury.
15. Name and give the formula of an important ore of (a) zinc; (b) copper; (c) lead; (d) tin; (e) nickel; (f) mercury.
16. Name six metals that occur free in nature.
17. Give three different and important uses of (a) zinc; (b) lead; (c) mercury; (d) copper.
18. What do gold and copper have in common besides being metals?
19. In what way is mercury unique among metals?
20. Outline the steps involved in obtaining a black-and-white photograph.
21. What is the per cent by weight of gold in 10-carat gold?
22. What is the per cent by weight of silver in German silver?

COLLATERAL READING

ELDER, SCOTT, and KANDA: "Textbook of Chemistry," Harper & Brothers, New York, 1948, Chapters 29, 31, 32, 33, and 34.

RICHARDSON and SCARLETT: "General College Chemistry," Henry Holt and Company, Inc., New York, 1947, Chapters 36, 38, 39, 40, 41, 42, 44, and 47.

SCHOCH, FELSING, and WATT: "General Chemistry," McGraw-Hill Book Company, Inc., New York, 1946, Chapters XXV and XXVI.

Iron and Steel. Alloys

IN THE PRECEDING chapter concerned with various metals, the impression may have been created in at least a few cases that the world was

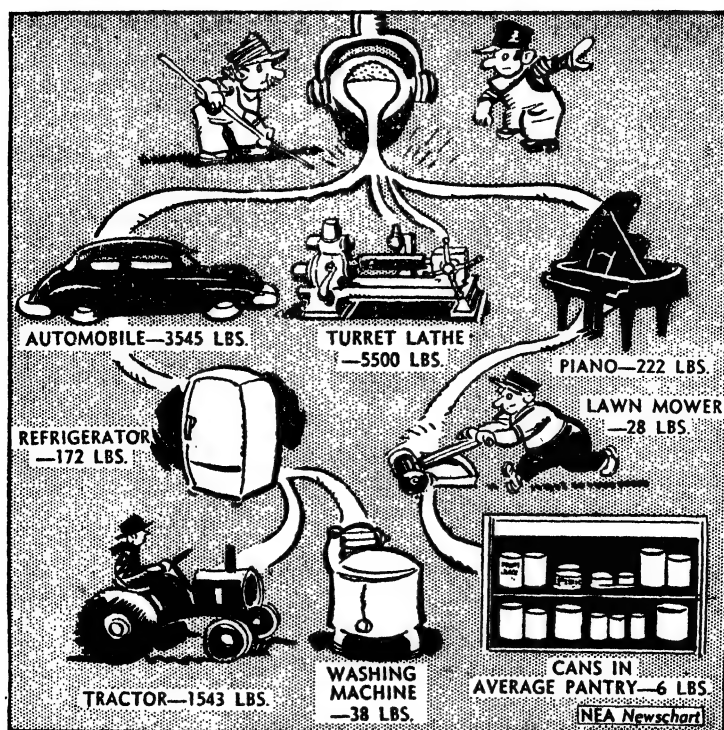


Figure 128. An indication of the importance of steel in everyday life.

critically dependent upon them. Of all the metals this comes more nearly being true of iron; for if the supply of iron were to decrease materially, there would be vast changes in our way of life.

The relative importance of iron in comparison with the other metals can easily be evaluated by looking at one's immediate surroundings and observing the kind and quantity of metals present. Figure 128 gives another illustration of the importance of iron by indicating the amount of iron (steel) in some common objects. Most countries that are industrially developed have readily available deposits of iron ore. It has



Figure 129. Open-pit mining of iron ore. (Courtesy of the Bethlehem Steel Co.)

been estimated that the present reserves of high grade iron ore in the United States will last until about 1963, and the low grade iron ore reserves will last until 2020.

The importance of iron in the world's economy is of recent origin, although iron has been known to man since a very early stage in history. This early use, though surprising in that iron is not found free in nature, is accounted for by the wide distribution of the compounds in which iron occurs and the ease with which they are decomposed to liberate the metal.

Iron occurs in nature in many different compounds, but only a few are suitable for use as a source of iron. To be of commercial value an iron ore must be relatively pure and available in large quantities. In the United States the only ore of importance is *hematite*, Fe_2O_3 , which

is found in very large amounts in the iron ranges of Michigan, Wisconsin, and Minnesota. Ores of lesser importance are *magnetite*, Fe_3O_4 ; *limonite*, $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$; *siderite*, FeCO_3 ; and *pyrite* (fool's gold), FeS_2 . The annual production of ore in the United States is around 100,000,000 tons, of which 90 per cent is hematite and the rest is magnetite and limonite.

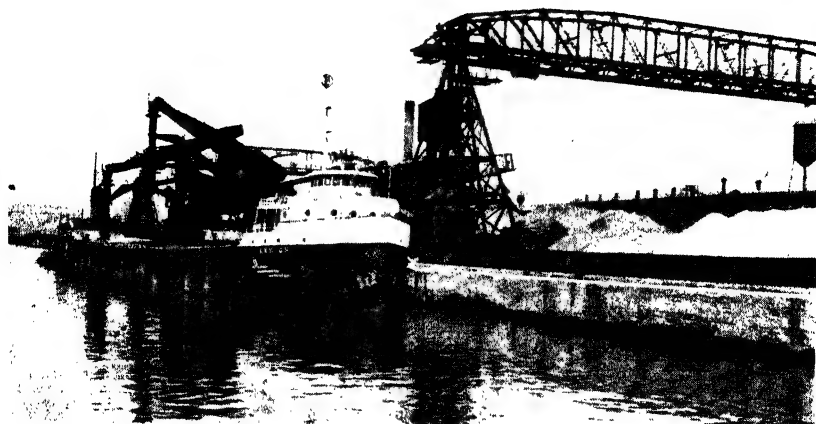
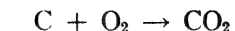


Figure 130. Unloading iron ore from a Great Lakes ore vessel. (Courtesy of the Bethlehem Steel Co.)

Metallurgy of Iron. The ore beds near the Great Lakes, which furnish about 85 per cent of the ore used in the United States, are strip-mined. *Strip mining* consists in removing the comparatively shallow top layer of soil, or overburden, and then simply digging the ore with large power shovels (Fig. 129). The ore is then shipped through the Great Lakes by boat (Fig. 130) to the iron and steel centers of the country for reduction to iron and fabrication into steel.

The chemistry involved in the production of iron from hematite is relatively simple. The raw materials required are limestone, coke (carbon), and the ore. Usually the ore contains sufficient sand to permit silicate formation; but if it does not, sand must also be added as a raw material.

The coke is burned to carbon, which in turn reacts with hot but unoxidized coke to form carbon monoxide.



The carbon monoxide then reacts with the ore to form iron and carbon dioxide.

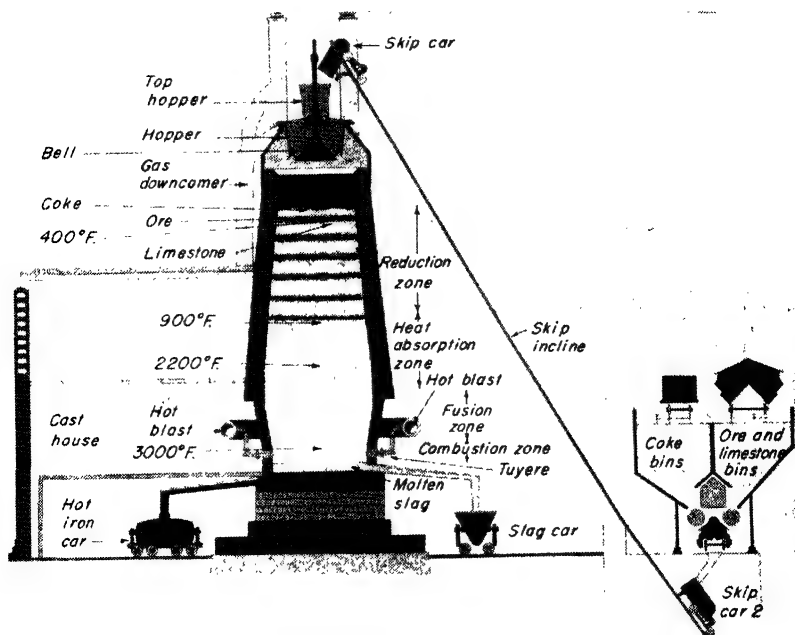
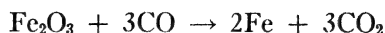


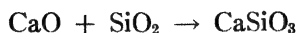
Figure 131. Blast furnace. (Courtesy of the Bethlehem Steel Co.)

The reaction actually takes place in steps depending upon the temperature, but the over-all result is the production of iron and carbon dioxide; an excess of carbon monoxide is always formed, however. The iron absorbs from 4 to 4.5 per cent of carbon and melts at about 1150°C.

At this high temperature the limestone decomposes to quicklime,



which reacts with the sand to form calcium silicate.



The apparatus used for the production of iron is called a *blast furnace* (Figs. 131 and 132). A typical blast furnace is 100 feet in height and 25 feet in diameter, with a capacity of 600 to 700 tons of iron per day. It is constructed of heavy steel plate and lined with fire-



Figure 132. Blast furnace. (Courtesy of the Bethlehem Steel Co.)

brick. The iron ore, coke, and limestone are added at the top of the furnace by means of a skip car. Hot air or oxygen is blown into the furnace through nozzles, or *tuyères*, at the bottom of the furnace, and some of the coke burns to generate heat, carbon monoxide, and carbon dioxide. The iron oxides are then reduced to iron, which melts and trickles down through the charge and collects in a pool on the furnace hearth. At the same time calcium silicate, or *slag*, is formed, and the molten slag drips to the hearth, where it floats on top of the heavier iron. For every ton of iron there is produced about one-half ton of slag.

The slag is drawn from the furnace at frequent intervals, hauled

away in large pots mounted on railway trucks, and dumped on the slag banks. Blast-furnace slag is used in the manufacture of cement and as ballast in road building, in concrete, and in similar applications as a replacement for crushed stone. An insulation material called *mineral wool* is made by blowing a jet of high-pressure steam through a stream of molten slag.

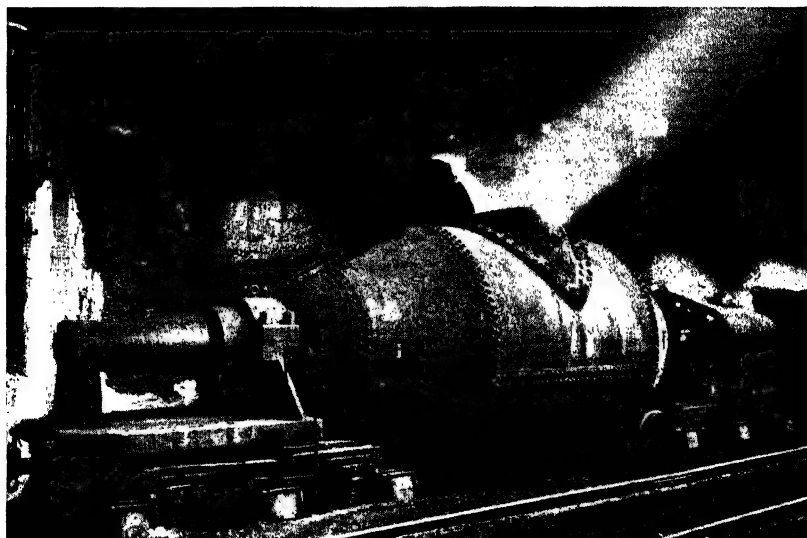


Figure 133. Hot-metal car being filled with molten pig iron from a blast furnace. (Courtesy of the Bethlehem Steel Co.)

In addition to iron and slag, a blast furnace produces about 6 tons of gas for every ton of iron. This gas, *blast-furnace gas*, is used as a fuel to heat the air used in the blast furnace and for various other heating purposes related to steelmaking.

One hundred to 150 tons of iron is tapped from a typical furnace every six hours and either run into molds to solidify or into hot-metal cars (Fig. 133), which haul the molten iron to large brick-lined vessels, where the iron is held in a molten condition until needed for making steel. The product of the blast furnace is called *pig iron* because in the past it was handled in the form of 40- to 100-pound bars, or pigs. In a modern steel plant the iron never cools from the time it is first heated in the blast furnace until it leaves in the form of structural steel, tin plate, rails, etc.

For the production of every ton of pig iron there is required one-half ton of limestone, one ton of coke, two tons of iron ore, and four tons of air. A recent development in the metallurgy of iron is the use of oxygen in place of air (Chapter 11). Only about one ton of oxygen is required per ton of iron produced, and much less than six tons of blast-furnace gas is formed. The waste involved in the use of air is the expense of heating large quantities of useless nitrogen.

Varieties of Iron. *Pig iron* is a relatively impure form of iron that contains (in addition to dissolved slag) about 2 to 4.5 per cent carbon, 1 to 2 per cent silicon, 0.1 to 0.3 per cent sulfur, 0.1 to 2.0 per cent phosphorus, and 0.2 to 1.0 per cent manganese. It is hard and brittle and has a low tensile strength and ductility.

Cast iron is produced when scrap iron is added to molten pig iron and the resulting mixture is allowed to cool in a suitable mold. The characteristics of the cast iron are determined by the rate of cooling. *White cast iron*, formed when the mixture is cooled rapidly, is hard and brittle and cannot be machined. *Gray cast iron*, which is softer and tougher than white cast iron and can be drilled and machined satisfactorily, is formed when the molten iron is cooled slowly.

If molten pig iron plus scrap iron is held at a temperature between 400 and 600°C. for several days and then slowly cooled, *malleable cast iron* results. Because this form of iron is tough and expands on cooling, it is used in the manufacture of stoves, machinery bedplates, radiators, and other articles not subject to shock during use. All cast iron can be easily broken by a sharp blow.

Wrought Iron. Wrought iron is produced from pig iron by heating it in a furnace along with nearly pure hematite ore. The oxygen in the hematite reacts with the impurities in the pig iron to form oxides of silicon, phosphorus, and manganese and volatile carbon dioxide and sulfur dioxide. The non-volatile oxides react with the lining of the furnace to form slag. As the impurities are removed, the melting point of the iron is raised until the iron is a semi-solid. At this point the iron is formed into large balls, or *blooms*, taken out of the furnace, and rolled into sheets.

Wrought iron is the purest iron made commercially, but it still contains about 1 per cent slag and one-tenth of 1 per cent carbon. The slag content is desirable because it is the slag that gives wrought iron its fibrous character and great tensile strength. Wrought iron can be forged and welded, and it is ductile and malleable. The principal uses

of wrought iron are in the manufacture of pipes, grate bars, nails, nuts, bolts, wire, chains, rails, etc.

Pure Iron. Pure iron is made by thermal decomposition of iron carbonyl in a process similar to that used in the production of pure nickel. It is not a commercial product except for special uses. Absolutely pure iron looks like silver and has many of the properties of silver.

Steel. Nearly the entire output of pig iron goes into the manufacture of steel. The lines of demarcation among cast iron, wrought iron, and steel are not distinct, at least from a chemical standpoint. There is, however, the following commercial or practical definition, which is very useful: *Steel* is essentially an alloy of the elements iron and carbon, the carbon content ranging from a few hundredths of 1 per cent to about 1.6 per cent. All steels contain varying but small amounts of manganese and silicon and very small quantities of phosphorus and sulfur.

Carbon content is the principal factor governing the type of steel—soft or mild steels contain one-tenth of 1 per cent carbon, and hard steels contain up to 1.60 per cent carbon. These steels are modified for special purposes by varying the amounts of manganese, silicon, sulfur, and phosphorus present; the alloy steels will be mentioned later in this chapter.

Essentially all steel is made by one of three methods, the Bessemer process, the open-hearth process, or the electric-furnace process.

The Bessemer Process. The Bessemer process for the production of steel was the first of three processes to be used commercially. It was discovered by William Kelly of Kentucky in 1847 and independently by Sir Henry Bessemer of England. Bessemer patented the process in 1855 and thus it bears his name, though rightfully it should be called the Kelly process. In this process the steel is made in a Bessemer converter, which consists of a pear-shaped vessel about 10 feet high, open at the top, and mounted on trunnions so that it can be tilted to receive the charge and to pour out the finished product (Fig. 134). A typical converter can handle 15 to 25 tons of pig iron at a time.

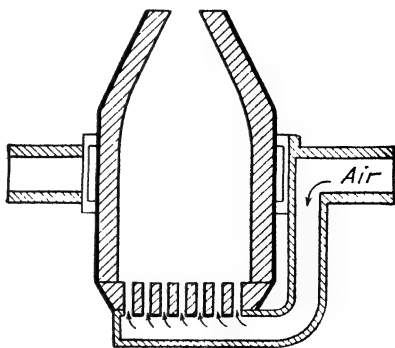


Figure 134. Bessemer converter.

The molten pig iron is added to the converter, and the material is blown with a blast of air introduced from the bottom through a number of small openings. The air oxidizes most of the impurities, which either burn out or form slag. After the "blow" the charge consists of nearly pure iron. The necessary amounts of carbon, silicon, and manganese are added to make the type of steel desired. The whole process

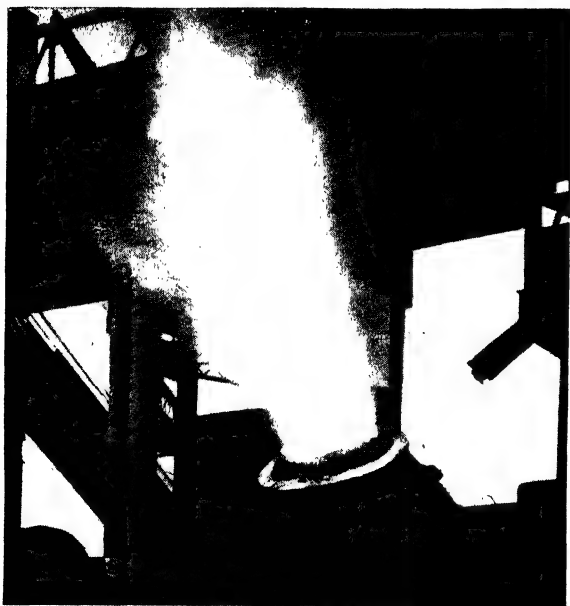


Figure 135. "Blowing" a Bessemer converter. (Courtesy of the Bethlehem Steel Co.)

takes only 20 minutes and constitutes one of the most spectacular operations in steelmaking (Fig. 135).

Only 10 per cent of the steel produced in this country is made by the Bessemer process, for the other two methods permit closer control of the products. Bessemer steel is used for certain types of wire and pipe.

The Open-hearth Process. Approximately 90 per cent of the steel produced in the United States is produced by the open-hearth process. The open-hearth furnace is shown schematically in Fig. 136. It is made of brick and steel and contains a saucer-like basin (hearth) capable of holding a charge of 100 to 175 tons of pig and scrap iron. A typical furnace is about 70 feet long and 20 feet wide. The furnaces

are heated by a direct flame from any of a number of gaseous fuels; the air is preheated in checker chambers under the furnace.

A typical charge to an open-hearth furnace will consist of 50 per cent cold scrap iron and steel and 50 per cent either cold or molten pig iron. Limestone to the extent of about 10 per cent of the total weight of metal is also added to assist in the formation of slag from the impurities present. Figure 137 shows the addition of scrap (foreground) and molten pig iron (background) to open-hearth furnaces.

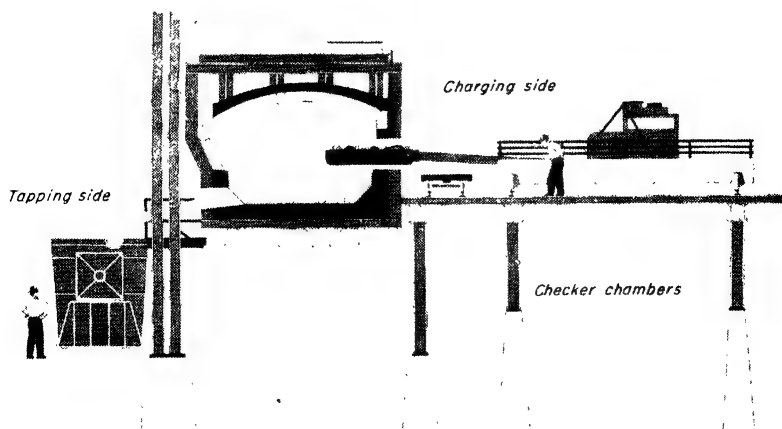


Figure 136. Open-hearth furnace. (*Courtesy of the Bethlehem Steel Co.*)

The charge is heated for about 12 hours, during which time the various impurities oxidize either to volatile oxides or to oxides, which form slag by reacting either with the calcium oxide (from the limestone) or with the basic lining of the furnace. The iron is analyzed periodically; and when it is of sufficient purity, the required amount of manganese, carbon, and silicon is added to give the desired type of steel. The furnace is then tapped, and the molten steel runs into a brick-lined steel ladle. The slag flows out last and spills over the filled ladle into an adjacent slag pot.

The composition of steel produced by the open-hearth process is subject to much more accurate analytical control than is possible in the Bessemer process, and consequently the steel is of better and more uniform quality. It is employed for all the multitudinous uses of steel.

Electric-furnace Process. Special steels, especially alloy steels, stainless steels, and tool steels, are made in electric furnaces because these furnaces permit operation in a neutral atmosphere and at carefully controlled temperatures. Electric furnaces are either of the arc type or the induction-heated type and hold from a few pounds to 75 tons or more (Fig. 138).

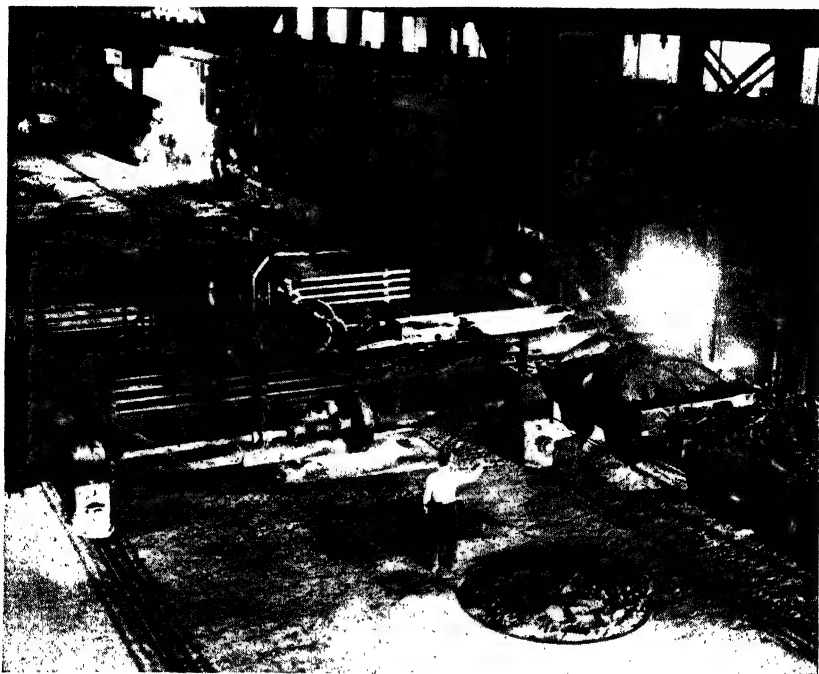


Figure 137. Charging steel scrap and molten pig iron (background) to open-hearth furnaces. (Courtesy of the Bethlehem Steel Co.)

Processing the Steel. The steel made by any of the foregoing processes is carried in a ladle to a pouring platform, where the steel is poured into cast-iron ingot molds. When the steel has cooled sufficiently to solidify, it is called an *ingot*. The molds are stripped from the ingots (Fig. 139), and the ingots are held in soaking pits until they are at a uniform temperature and ready for mechanical forming in the hot-rolling mills.

The hot steel ingots are processed by rolling, hammering, or pressing; this hot mechanical working improves the physical properties of the steel. The more economical rolling process far exceeds the other two



Figure 138. A 50-ton electric furnace for the production of steel. (*Courtesy of the Bethlehem Steel Co.*)

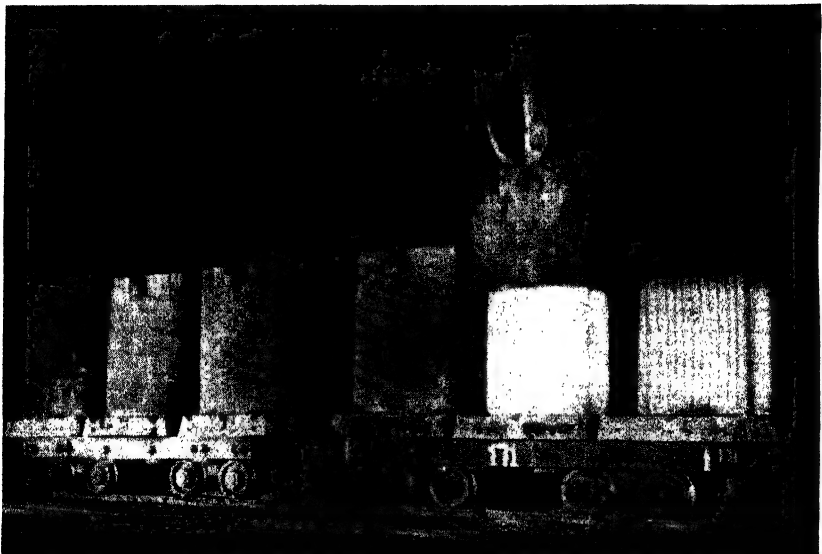


Figure 139. Molds being stripped from solidified steel ingots. (*Courtesy of the Bethlehem Steel Co.*)

methods from the standpoint of tons of steel processed. As the name implies, the rolling operation consists in passing the hot plastic steel between rolls (Fig. 140), which reduces the large ingots to smaller

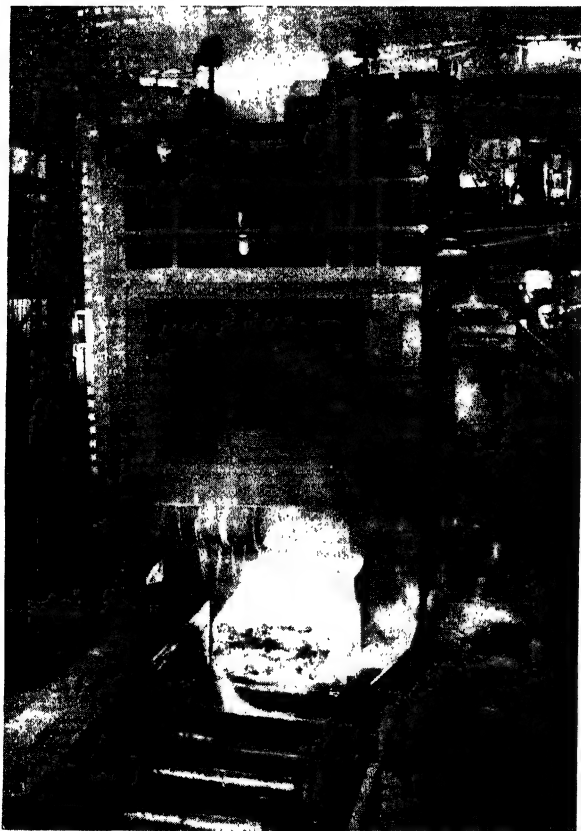


Figure 140. Rolling in the ingot, the first step in the mechanical working of steel. (*Courtesy of the Bethlehem Steel Co.*)

sizes and shapes them into sheets or simple structural forms such as rounds, squares, rectangles, etc. Some of the operations are very rapid. Thin steel sheet (strip steel), for example, is finished at the rate of 25 miles per hour, and 600 to 700 feet is coiled and ejected in 20 seconds.

Compounds of Iron. Only a few of the compounds of iron are of economic value other than as sources of iron. Perhaps the most im-

portant is iron oxide, Fe_2O_3 , which is the oxide formed when iron rusts. It is used as a red pigment in paint (barn paint), and in a slightly different form it is known as *rouge*. The common variety of blue-black ink contains complex iron salts, and the process of making blueprints also utilizes complex iron salts.

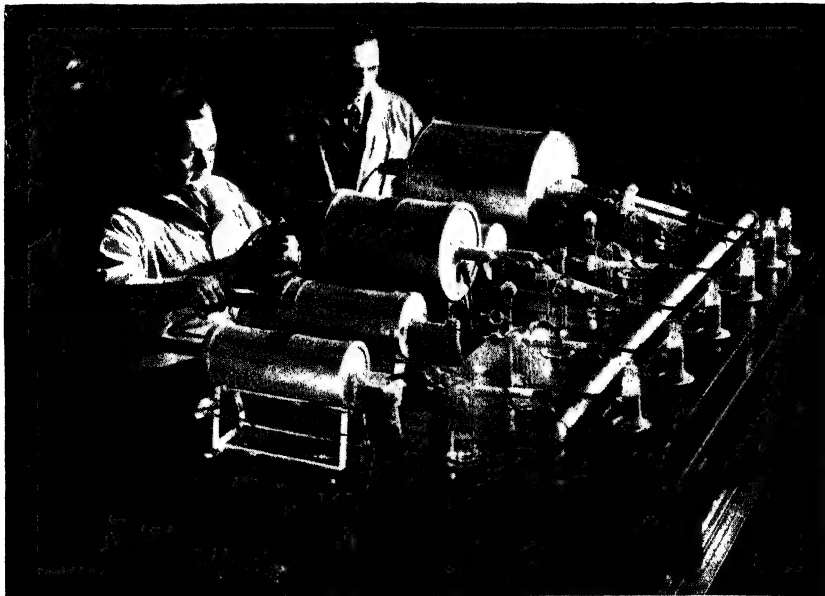


Figure 141. Combustion analysis of alloy steel in a steel-plant chemical laboratory. (Courtesy of the Bethlehem Steel Co.)

ALLOYS

The development of the automobile industry led to many changes in the steel industry as well as changes in the more personal phases of economics. One of these changes was the development of alloy steel designed to meet the need for metal parts that would withstand shocks and strains, resist corrosion, retain hardness at high temperature, etc. Not only have many different alloy steels been developed but also many other types of alloys used for special purposes.

It has been mentioned previously (Chapter 20) that *alloys* are obtained by melting two or more metals together and then allowing the resulting mixture to cool and solidify. In general, the properties of an

TABLE 8. Some Common Alloys

<i>Name</i>	<i>Alloyed metal, %</i>	<i>Properties</i>	<i>Uses</i>
Iron (steel):			
Stainless steel.	Cr (15)	Resistant to corrosion	Manufacture of ornamental parts of automobiles, etc.
Nickel steel.	Ni (2-5)	Stainless, very hard, yet elastic	Gears, shafting, wire rope
Invar steel.	Ni (36)	Non-expanding	Clocks, pendulums, tapelines, etc.
Manganese steel.	Mn (10-18)	Very hard; resists abrasive wear	Safes, railroad frogs, teeth on elevator dredges
Tungsten steel.	W (10-20)	Remains hard at high temperatures	Cutting tools, high-speed drills
Chrome-vanadium steel	Cr (1-9) V (0.15-0.2)	Resists fatigue, has high tensile strength	Automobile parts; springs, axles, etc.
Chrome-nickel steel	Ni (1-5) Cr (1-2)	Great hardness; high tensile strength	Armor plate for battleships and tanks
Molybdenum steel.	Mo (0.3-3)	Hard, heat-resistant	Axles
Chrome steel.	Cr (2-4)	Very hard; resistant to shock	Files, ball bearings, safes, etc.
Copper:			
Beryllium copper.	Be (2.0)	Resistant to fatigue	Springs, non-sparking tools
Cartridge brass.	Zn (30)		Radiators, shells
Naval brass.	Zn (39.25) Sn (0.75)	Resistant to sea water; takes high polish	Tubeheads, ship brass
Nickel silver.	Zn (20) Ni (15)	Looks like silver	Key stock, table silver
Manganese bronze.	Zn (41); Fe (1); Al (1); Mn (0.5)	Corrosion-resistant and long-wearing	Propeller blades
Nickel:			
Monel metal.	Cu (28)	Corrosion-resistant, bright surface	Food industries, kitchen fixtures, shipboard use
Permalloy.	Fe (22)	High magnetic susceptibility	Telephones, ocean cables
Nichrome.	Cr (40)	High melting point, low electrical conductivity	Wire in electrical heating units, stoves, toasters, etc.
Aluminum:			
Duralumin.	Mn (5.5); Cu (4); Mg (0.5)	Light; high tensile strength	Airplane and automobile parts, etc.
Magnalium.	Mg (5-30)	Light	Scientific instruments
Lead:			
Shot metal	As (1)	Harder than lead, yet readily fusible	Bullets and shot
Bismuth:			
Wood's metal.	Pb (31); Cd (16); Sn (15)	Low melting point (70°.)	Automatic sprinklers, fuse plugs

alloy are quite different from those of either or any of the component metals. An alloy may melt at a temperature higher or lower than the melting points of any of its constituent elements. It is generally true that an alloy is harder and a poorer conductor of electricity than any of its components.

Alloys are commonly more resistant to corrosion than pure metals, and it is for this reason that they are so widely used by the chemical and petroleum industries in the construction of equipment. The colors of alloys usually cannot be predicted from the color of the component metals. For example, the 5¢ coin contains considerable copper but looks like nickel, and certain alloys of silver and gold are green in color.

Owing to the large number of metals and the almost infinite number of combinations possible, it is apparent that the production of alloys offers a fruitful field for future investigation.

The composition of a few common alloys not mentioned previously in Chapter 20 is given in Table 8. Owing to the importance of alloy steels, these alloys are given more prominence than those which contain a preponderance of other metals.

EXERCISES

1. *New terms:* strip mining, pig iron, malleable cast iron, steel, electric-furnace process, slag, white cast iron, wrought iron, Bessemer process, ingot, blast-furnace gas, gray cast iron, blooms, open-hearth process, rouge, mineral wool.
2. List by name the iron and steel objects in your study room.
3. Give four uses for blast-furnace slag.
4. What is the difference between ordinary barn paint and rouge?
5. Make four generalizations pertaining to the relationship between the physical properties of an alloy and the physical properties of its component metals.
6. Account for the fact that iron was used at an early period in history yet did not occur free in nature.
7. Why is it desirable for casting metal to expand on cooling?
8. Give two examples of alloys that possess a color different from at least one of their components.
9. What type of steel would one use for tableware?

10. Give the names and formulas of the three iron ores used in the United States. Which of these ores accounts for the greatest amount of iron?
11. What three processes are used for the production of steel from pig iron? Which of these methods is the most important?
12. Write equations representing five reactions that take place in a blast furnace.
13. Outline the steps involved in producing a steel rail from ore mined in Minnesota.
14. Why is the development of alloys of great importance to our economy?
15. How much silver is there in nickel silver?
16. List by name the impurities in pig iron.
17. If 75 tons of pig iron is charged to a typical open-hearth furnace, how many tons of scrap iron and limestone are also added?

COLLATERAL READING

- ELDER, SCOTT, and KANDA: "Textbook of Chemistry," Harper & Brothers, New York, 1948, Chapters 29 and 35.
- HOLMES: "Introductory College Chemistry," The Macmillan Company, New York, 1946, Chapters XLII, XLV, and XLVI.
- RICHARDSON and SCARLETT: "General College Chemistry," Henry Holt and Company, Inc., New York, 1947, Chapter 39.
- SCHOCH, FELSING, and WATT: "General Chemistry," McGraw-Hill Book Company, Inc., New York, 1946, Chapters XXV and XXVII.

Non-metals

THE OTHER great class of elements, the non-metals, is in some respects not as well known as the metals. The lack of familiarity with the non-metals is associated with the fact that their compounds are, in general, more important than the uncombined elements. There are, however, some elemental non-metals which occur in nature and which are important. Of these, oxygen, nitrogen, and the inert gases have already been mentioned in their relation to the atmosphere. Nitrogen, sulfur, phosphorus, and the halogens (fluorine, chlorine, bromine, and iodine) will be discussed in this chapter along with some of their more important compounds.

Before discussing some of the individual non-metallic elements it will be profitable to summarize the general characteristics of non-metals, especially in contrast to the metallic elements.

The physical properties of the non-metals present more striking contrasts than do those of the metals. The non-metals range from helium, which boils at $-267^{\circ}\text{C}.$, to carbon, which melts at about $3500^{\circ}\text{C}.$ Of the predominantly non-metallic elements, seven are solids, one is a liquid, and ten are gases under ordinary atmospheric conditions. Obviously their densities vary tremendously.

Among the solid non-metals it is frequently found that the same element is capable of existing in different physical forms. The most spectacular example of this phenomenon is the element carbon, which may exist as the crystalline diamond or the amorphous wood charcoal. In all cases the different forms of the elements have essentially the same chemical properties. Both diamond and charcoal burn to form carbon dioxide. These different physical forms of the same element are known as *allotropic forms*.

Metals have been characterized as the elements which form the positive portion (cation) of a compound; it follows that the non-metals are those elements which form the negative portion (anion).

The non-metals usually have four or more electrons in their outer electron shell and have a tendency to gain more electrons to complete this shell. This gain of electrons may be by sharing electrons or by outright acquisition. Non-metals show a variable valence, as many as three or four important valence states being exhibited by a single element.

Another important chemical characteristic of non-metals is that their binary compounds with oxygen or hydrogen will react with water to form acidic compounds. The non-metals are acid-forming elements.

Sulfur. Sulfur (sulphur) is another of those elements which has been mentioned in writings from the earliest to the present time. Sulfur is the *brimstone* of the Bible, and it was used as a disinfectant in the time of Homer. The alchemists were much interested in sulfur, because it burned readily and, when burning, gave off pungent fumes. It was not until the nineteenth century that sulfur was recognized as an element.

Occurrence. Sulfur occurs in nature in the elemental state and in the form of both organic and inorganic compounds. The inorganic compounds are generally sulfides and sulfates, while the organic compounds are constituents of many of our foods. The most important sulfides are those used as ores (Chapter 20), and consequently they are of value more for the metal associated with the sulfur than for the sulfur itself. *Pyrite*, FeS_2 , is the only sulfide mined for the sulfur it contains. It is estimated that the ocean contains eleven hundred trillion tons of sulfur in the form of sulfates; sulfates, however, are not used at present as a source of sulfur. The more important sulfates were mentioned in Chapter 16.

Fairly large deposits of elemental sulfur associated with volcanic vents are found in Japan and Chile. Smaller but more interesting deposits of sulfur are found encrusting hot springs such as the Mammoth Hot Springs in Yellowstone Park. Over 95 per cent of native sulfur, however, is obtained from gypsum and limestone formations above salt domes, and enormous deposits of sulfur in formations of this type are located along the Gulf coast of the United States. Lesser deposits of the same type occur in Sicily. The present known deposits of sulfur in the United States are estimated to be sufficient to last until about 1985.

Production. Until the start of the twentieth century most of the world's supply of sulfur came from Sicily. The great sulfur deposits of

the United States were known, but no practical method of utilizing them was available. These deposits are 500 to 1500 feet underground, the ground is usually marshy and saturated with hydrogen sulfide (a poisonous gas), and as a consequence ordinary mining methods could not be used.

The problem was solved by Herman Frasch in 1891, but it took twelve years for him to prove that his solution was a practical one. The *Frasch process*, as he developed it and as it is used today, depends upon the fact that sulfur melts at a temperature only slightly greater than that of boiling water. He proposed to drill a well, melt the sulfur with superheated water (160 to 170°C.), and force the molten sulfur to the surface with compressed air.

Figure 142 gives a diagrammatic picture of a modern well which is substantially of the same design as that developed earlier by Frasch. Of the three concentric pipes, the outer 6-inch pipe is used to send hot water into the well, the 3-inch pipe is the sulfur line through which the melted sulfur goes to the surface, and the inner 1-inch pipe is for compressed air. At the surface the molten sulfur is pumped through steam-jacketed pipes to a central solidification vat (Fig. 144) that may hold more than a half million tons of sulfur. A single well can produce 400 to 500 tons of sulfur per day. The sulfur obtained by the Frasch process is 99.5 to 99.95 per cent pure.

Sulfur exists in two allotropic crystalline forms and two allotropic liquid forms. *Flowers of sulfur* are very fine and usually very pure crystals of sulfur.

Uses. Sulfur is often considered one of the four basic raw materials of the chemical industry (the other three are salt, coal, and limestone). The uses of sulfur may be divided into those which employ elemental sulfur and those which utilize compounds made from it. About 80 per cent of the sulfur is burned to sulfur dioxide, SO_2 , which in turn is used to make other compounds, some of which will be mentioned in the section pertaining to compounds of sulfur.

Elemental sulfur is employed in the manufacture of nearly all rubber goods, a use mentioned where rubber is discussed in Chapter 26. Sulfur is also used in the form of a fine powder to kill plant pests, it is an ingredient, along with charcoal and potassium nitrate, in black gunpowder, and it finds some utilization as a cementing agent.

Compounds of Sulfur. Compounds of sulfur are employed in the

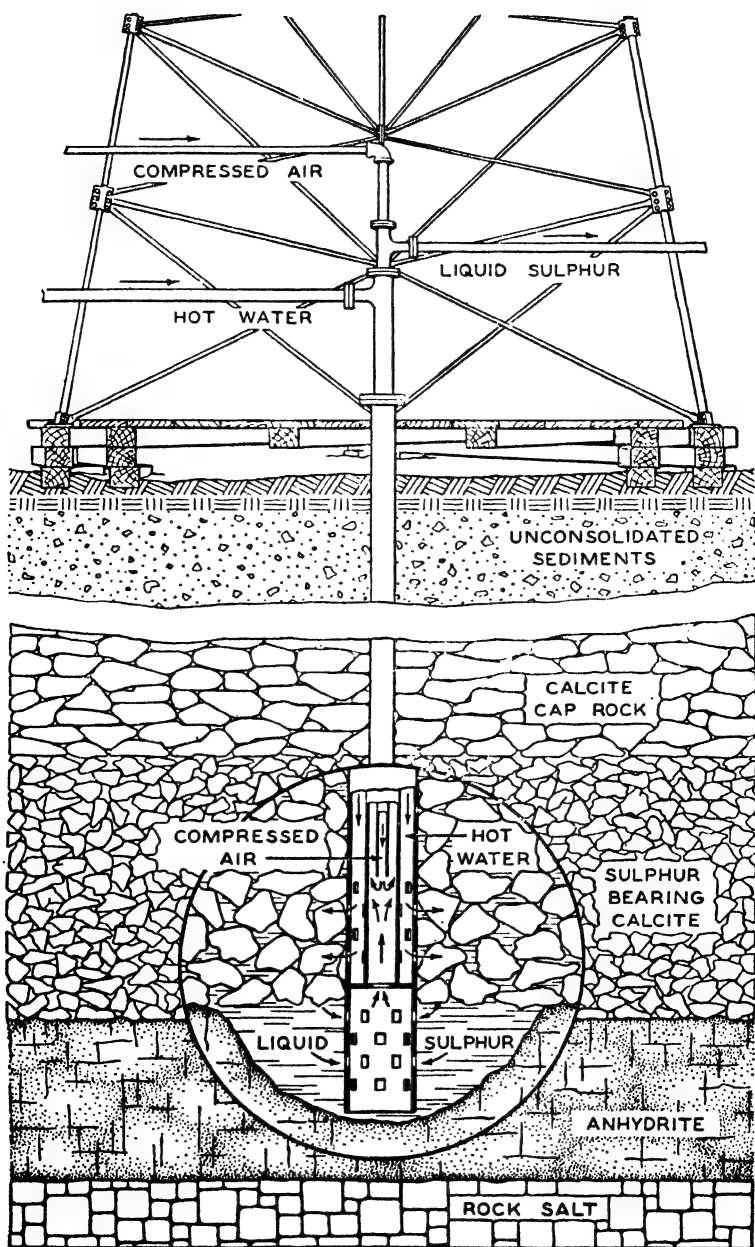


Figure 142. Diagrammatic picture of a sulfur well. (Courtesy of the Texas Gulf Sulphur Company.)

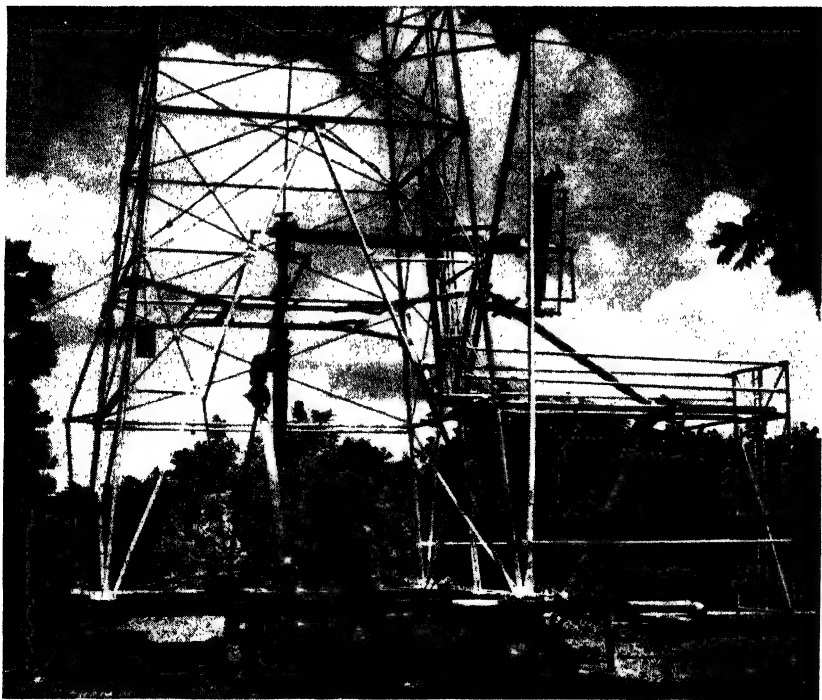


Figure 143. The surface equipment of a sulfur well. (*Courtesy of the Texas Gulf Sulphur Company.*)



Figure 144. Sulfur being discharged into a vat. (*Courtesy of the Texas Gulf Sulphur Company.*)

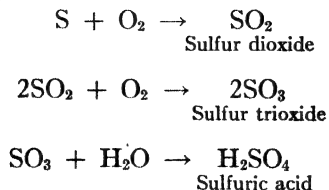
manufacture of nearly all consumers' goods. Most of these compounds are made either directly or indirectly from *sulfuric acid*, H_2SO_4 . For this reason sulfuric acid production has frequently been suggested as a measure of national prosperity: "Tell me the amount of sulfuric acid produced, and I will tell you the country's importance as an industrial nation." There seems to be a close relationship between the total pro-



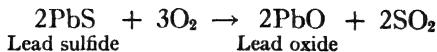
Figure 145. Sulfur ready for shipment. (Courtesy of the Texas Gulf Sulphur Company.)

duction of sulfuric acid and the gross national product and income.

Sulfuric acid is produced by two different processes, the contact process and the lead-chamber process. The basic reactions are the same in each process.



The sulfur dioxide may come from the burning of sulfur or by the roasting of a sulfide ore, for example, the roasting of lead sulfide.



In the *contact process* the sulfur dioxide and air are passed over a catalyst of either platinum metal or vanadium pentoxide, V_2O_5 , in an apparatus similar to that shown diagrammatically in Fig. 146. The sulfur dioxide is oxidized to sulfur trioxide, which is then absorbed in concentrated sulfuric acid. Water is added to the acid containing the sulfur trioxide, and more sulfuric acid is formed, the amount of water

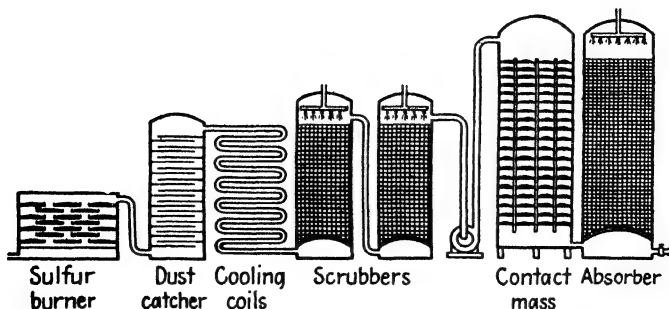


Figure 146. The contact process for the production of sulfuric acid.

added governing the concentration of acid produced usually 96 per cent acid.

The contact process produces a concentrated acid of high purity. The disadvantages of this method for the production of sulfuric acid are the high cost of the catalyst and the fact that, if sulfides are used as the source of the sulfur dioxide, costly purification of the dioxide is necessary because impurities will render the catalyst inactive.

The lead-chamber process utilizes sulfur dioxide from either sulfur or sulfides without further purification and oxidizes the dioxide to the trioxide under the catalytic influence of oxides of nitrogen (Fig. 147). Sulfur dioxide, oxides of nitrogen, and air are mixed and enter a lead chamber along with steam. Both the oxidation of the sulfur dioxide and the reaction between the sulfur trioxide and the water take place in this and subsequent chambers. The sulfuric acid collects in the bottom of the lead chambers.

The lead-chamber process is more economical than the contact process, but it produces a more dilute acid (75 per cent) and a less pure acid. Few if any new lead-chamber sulfuric acid plants are constructed

because most of the uses of sulfuric acid require an acid of high purity and concentration. The only important use of lead-chamber acid is in the manufacture of fertilizers (Chapter 31).

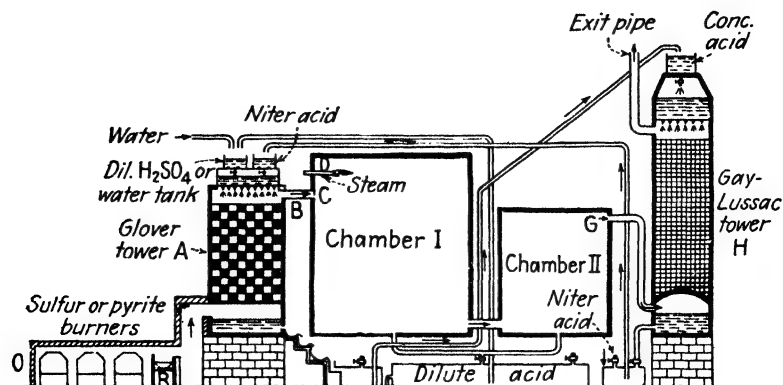
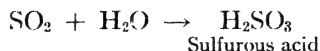


Figure 147. The lead-chamber process for the production of sulfuric acid.

Approximately 10 million tons of 100 per cent sulfuric acid is produced each year, and its uses are distributed as follows:

Superphosphate fertilizers	29%
Chemicals	22%
Petroleum refining	15%
Paint and pigments	8%
Explosives (non-ordnance)	8%
Iron and steel pickling	6%
Rayon and cellulose film	5%
Metallurgical uses other than for iron and steel	3%
Miscellaneous	4%

In addition to the use of *sulfur dioxide* for the production of sulfuric acid it is employed to produce sulfurous acid, which in turn is used in large quantities by the pulp and paper industry.



Sulfur dioxide is also used to bleach silk, straw, wool, and other fabrics and as a refrigerant liquid in refrigeration units.

Carbon disulfide is made by the reaction between carbon and sulfur at a high temperature.



It is used as a solvent and in the manufacture of rayon and cellophane and a number of other products. Carbon disulfide is highly flammable and toxic and, because of this latter property, is used as a fumigant. *Hydrogen sulfide*, H_2S , is the odoriferous gas that gives both chemistry laboratories and rotten eggs their characteristic aroma. Used in chemistry in qualitative analysis, it causes many metal ions to precipitate from solution as the sulfides, and these frequently have characteristic colors.

The inorganic sulfur compounds not already mentioned are of lesser importance, and space will not permit their inclusion in the present discussion.

Nitrogen. Nitrogen is a component of compounds (proteins — meat) related to all living matter, and consequently it is an element essential to life. Only a few elements are as important as or more widely used than nitrogen; it is fortunate that there is an unlimited amount of nitrogen in the atmosphere. The problem of changing the nitrogen in the air into compounds usable by plants and animals, however, was solved by man only within the last thirty-five years.

Long before man made his presence known on earth, nature had solved the problem by developing bacteria that have the ability to transform, or “fix,” atmospheric nitrogen into protein compounds and nitrates. These bacteria live in the nodules on the roots of legumes such as peas, beans, clover, and soybean (Fig. 148). Some atmospheric nitrogen is also “fixed” during thunderstorms by the lightning causing a reaction between the oxygen and nitrogen to form oxides of nitrogen. This source alone furnishes more than 5 pounds of nitrogen compounds per acre each year.

In nature the nitrogen goes into the plants in the form of proteins. The plants are eaten by animals, and the nitrogen compounds become flesh or meat. The animal dies, and in the course of the subsequent decomposition the proteins liberate nitrogen to the air. This over-all process is known as the *nitrogen cycle* and accounts for the fact that during a few billion years the nitrogen content of the air has remained reasonably constant.

The methods developed by man to add nitrogen compounds to the soil are of great interest and will be discussed in detail in Chapter 31.

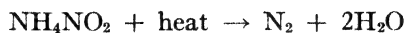
Pure nitrogen is a tasteless, odorless, and colorless gas that does not

support combustion. Chemically it is classed as unreactive but not inert; *i.e.*, it will react but only under rather severe conditions.



Figure 148. Soybean roots with nodules of nitrogen-fixing bacteria. (*Courtesy of the U.S. Department of Agriculture, Bureau of Plant Industry.*)

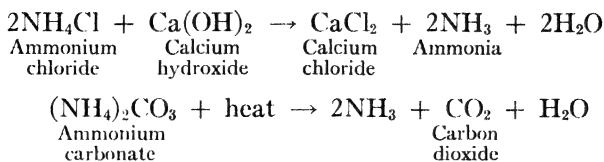
Pure nitrogen is prepared on a laboratory scale by the decomposition of ammonium nitrite.



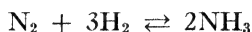
Industrial nitrogen, which may be 99.99 per cent pure but usually is 95 to 99 per cent pure, is prepared by the distillation of liquid air. The most important use of nitrogen is for the preparation of ammonia.

Ammonia, NH_3 , is second only to water in importance among the

simple hydrogen compounds. It is prepared in the laboratory by a number of different reactions. For example, .



Industrially, ammonia is made by the *Haber*, or *synthetic ammonia*, *process*, which is based upon the following reaction:



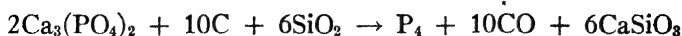
This is an equilibrium reaction, and under normal conditions only a very small amount of ammonia is formed. An economic amount of ammonia is produced only at temperatures of 400 to 600°C. and at pressures between 3000 and 15,000 pounds per square inch. Even under these drastic conditions a catalyst is necessary to make the process practical.

Ammonia is used as a refrigerant and as a fertilizer. Great quantities of ammonia are used in the manufacture of nitric acid, sodium bicarbonate, sodium carbonate, various ammonia compounds employed as fertilizers, and other useful chemicals.

Nitric acid, HNO_3 , is produced from ammonia by first oxidizing it with air in the presence of a silver or platinum gauze and then causing the oxides thus formed to react with water. The nitric acid produced in this manner is about 50 per cent HNO_3 . Nitric acid is used in the manufacture of explosives for both war and peace (Chapter 28), dyes (Chapter 28), medicinals (Chapter 30), and many other compounds. Most of the organic and inorganic nitrogen compounds of commerce are made from ammonia with nitric acid as an intermediate.

The important inorganic nitrogen compounds that occur in nature have been noted in Chapter 16.

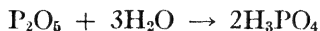
Phosphorus. Phosphorus occurs in nature only in compounds, mainly as the mineral *phosphorite*, $\text{Ca}_3(\text{PO}_4)_2$, which in an impure form is called *phosphate rock*. Phosphorus is prepared in the elemental form by heating a mixture of sand, coke, and phosphate rock in an electric furnace.



The phosphorus distills out of the furnace and is liquefied and cast into sticks under water.

Solid phosphorus exists in two allotropic forms. *White* (yellow) *phosphorus* is a translucent, wax-like solid that melts at 44°C. It is highly flammable and very poisonous. *Red phosphorus* has a metallic appearance, and it is non-flammable. White phosphorus by reaction with atmospheric oxygen is used in chemical warfare for the production of smoke screens. The phosphorus is liberated from shells, grenades, or bombs and is oxidized to form finely divided particles of P_2O_3 and P_2O_5 . White phosphorus is also used as an antipersonnel weapon and as an incendiary material. The greater part of the phosphorus produced in the United States is used in the manufacture of *phosphor bronze*.

Phosphoric acid is prepared by hydrating phosphorus pentoxide.



Phosphoric acid is used to make other compounds such as high-grade phosphate fertilizers and chemicals for baking powders, water-softening agents, etc. The free acid is used in many soft drinks.

Phosphorus is one of the three elements (nitrogen and potassium are the other two) that in the form of compounds must be added to soil to ensure continued normal plant growth. The role of phosphorus compounds as fertilizers will be discussed in the chapter concerned with the relationship of chemistry to agriculture (Chapter 31).

Matches. The head of a modern "strike-anywhere" match is composed of a mixture of potassium chlorate ($KClO_3$), paraffin, glue, and finely ground glass. The tip of the match head contains some phosphorous sesquisulfide (P_4S_3). When the match is "struck," the P_4S_3 ignites from the heat generated by the friction. The burning P_4S_3 ignites the $KClO_3$, which in turn causes the paraffin to burn, and finally the wood.

Safety matches have a head composed of potassium chlorate (a source of oxygen), antimony trisulfide (Sb_2S_3), the combustible material, and glue. This mixture is not readily ignited by friction, but it will ignite easily if drawn across a side of the matchbox, which is coated with a mixture of red phosphorus, ground glass, and glue.

THE HALOGENS

The halogens—fluorine, chlorine, bromine, and iodine—comprise the main family of periodic Group VII. From this fact alone, considerable

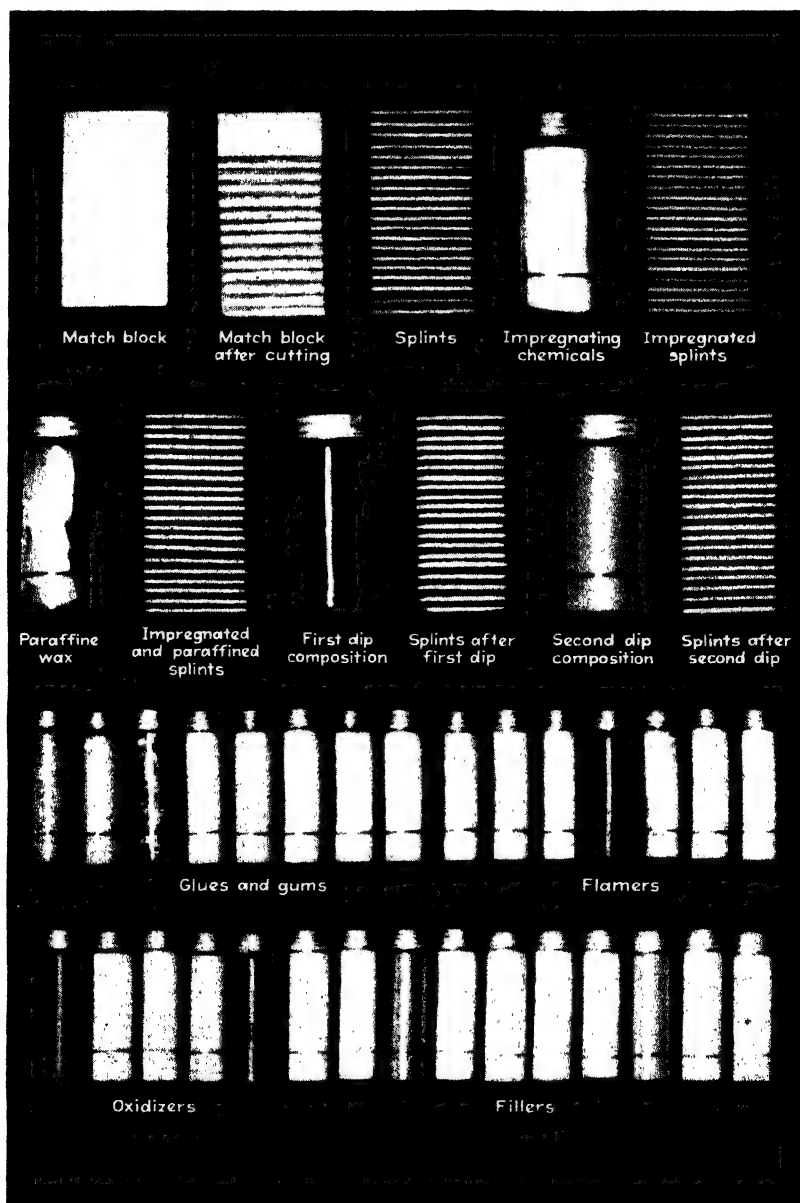


Figure 149. Steps in the preparation of matches. (Courtesy of The Diamond Match Company.)

information is given as to their chemical and, to a lesser extent, their physical properties. These relationships were pointed out during the discussion of the periodic table (Chapter 5), and they should be reviewed and kept in mind during the following description of the properties of the individual halogens and their various compounds.

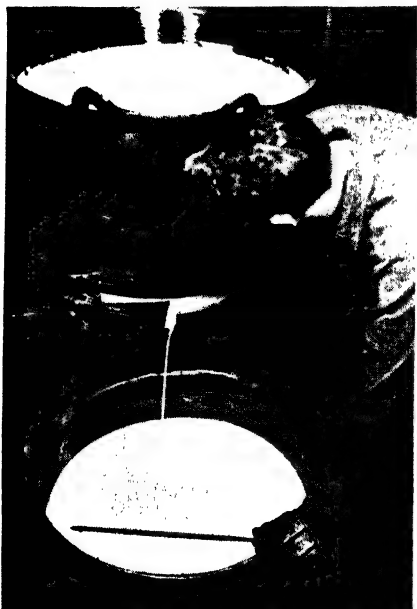


Figure 150. Grinding match composition. (Courtesy of The Diamond Match Company.)

The halogens do not occur in nature in the elemental state, owing to their great reactivity.

Fluorine. Fluorine is the lightest and most reactive of the halogens; in fact, it is the most reactive of all the elements. It is fairly abundant in the form of minerals such as *fluorspar*, CaF_2 ; *cryolite*, Na_3AlF_6 , and *fluorapatite*, $\text{CaF}_2[\text{Ca}_3(\text{PO}_4)_2]_3$.

Fluorine was the last of the halogens to be produced in the elemental state although many chemists tried to obtain the element from its compounds. Several chemists lost their lives from the effects of working with fluorine. It was not until 1886 that Henri Moissan finally succeeded in making fluorine by the electrolysis of potassium fluoride,

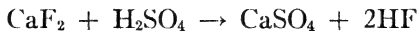
KF, in liquid hydrogen fluoride, HF.

Fluorine is prepared commercially by the electrolysis of fused potassium hydrogen fluoride, KHF_2 . Its principal uses are in the preparation of other compounds, the most notable being associated with the separation of uranium isotopes. The volatile *uranium hexafluoride*, UF_6 , was made and fluorides of the two isotopes of uranium (U^{235} and U^{238}) were separated by physical means depending upon the difference in weight of the two fluorides. Other fluorine compounds were also made for special purposes related to the same general project.

The use of cryolite in the production of aluminum has already been

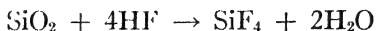
mentioned, and several fluorine-containing organic compounds will be noted later. Sodium fluoride is used as a flux, as an insecticide, and as a wood preservative.

Hydrogen fluoride is prepared by the action of sulfuric acid on calcium fluoride.



Hydrogen fluoride boils at 19°C. and is used in both the liquid and the gaseous state. It is used as a catalyst in the preparation of aviation gasoline and for the preparation of a number of fluorine compounds.

One of the most interesting chemical properties of HF is its ability to react with silica and silicates to form volatile silicon tetrafluoride, SiF_4 .



Because glass is a mixture of silica and silicates, HF dissolves, or "etches," glass.

Hydrogen fluoride causes very serious burns that take many months to heal. It was usually hydrogen fluoride that injured and killed the early workers in the field, although fluorine is also very toxic.

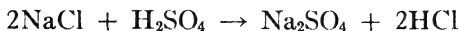
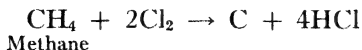
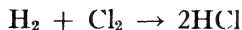
Chlorine. The occurrence of chlorine in the form of various chlorides has already been cited in relation to the metals associated with the chlorine.

Chlorine may be produced in the laboratory by various methods, but in general it is purchased in cylinders because of the low cost and convenience. The commercial production of chlorine has been discussed in connection with the electrolysis of fused sodium chloride and aqueous sodium chloride (Chapter 19). The first commercial production of chlorine in the United States was at Rumford Falls, Maine, in 1893; the current annual production of chlorine is over 1.5 million tons.

Chlorine is a yellow-green gas with a pungent odor. It is used in the sterilization of drinking water, etc., and for the bleaching of wood pulp. Over 75 per cent of the chlorine produced is used for the manufacture of hundreds of organic compounds, some of which will be mentioned in the chapters devoted to organic chemistry.

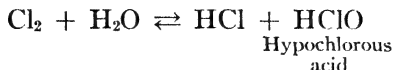
Hydrogen chloride is prepared by the direct reaction between hydro-

gen and chlorine, methane and chlorine, and by the reaction between sodium chloride and sulfuric acid.



Hydrogen chloride is a gas that is very soluble in water, in which it dissolves to form *hydrochloric acid*. Hydrochloric acid is only slightly more expensive than sulfuric acid, and it is used for many purposes where an acid is needed. For example, it is employed to remove rust from iron (pickling) and to hydrolyze starch and wood to sugars. About 100,000 tons is used each year.

Hypochlorous acid is formed when chlorine is dissolved in water.



Hypochlorous acid and its salts are relatively unstable and decompose to liberate oxygen. Owing to this property, these compounds are strong oxidizing agents. They are used as bleaching agents (Purex, Chlorox), antiseptics, and disinfectants and in the production of certain organic compounds.

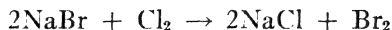
A calcium salt of hypochlorous acid [$\text{CaCl}(\text{ClO})$] is known as *bleaching powder* or “chloride of lime,” and another calcium salt [$\text{Ca}(\text{ClO})_2$] is called **HTH**, which is short for “high-test hypochlorite.”

Potassium chlorate, KClO_3 , is used in the manufacture of matches, fireworks, and explosives. The sodium salt is sometimes employed as a weed killer.

Bromine. Bromine was discovered independently in 1825–1826 by two chemists in their early twenties. The name of *muride* was given to the new element, but later the young men were overruled by the august French Academy of Science, which preferred *bromine* from the Greek word meaning “bad odor” or “stench.” Bromine has other distinguishing characteristics besides its unpleasant odor. It is one of the very few liquid elements (boiling point, $59^\circ\text{C}.$), and it is highly colored—a reddish brown. Most of the elements are colorless or “silvery” in color.

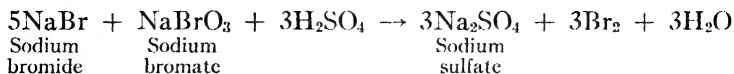
The occurrence of bromine parallels that of chlorine, and it is prepared commercially from bromides obtained from salt-well brines and from sea water. The ocean contains only about 0.0065 per cent bromine, in the form of bromides, but this concentration is sufficient to provide about 300,000 tons of bromine per cubic mile of sea water. The magnitude of a cubic mile may be appreciated from the facts that a cubic mile of sea water weighs 4 billion tons and that a box of these dimensions will more than hold the entire human race.

Bromine, like chlorine, is only infrequently prepared in the laboratory because it is more convenient to purchase it. The basic reaction involved in the commercial production of bromine from sea water is



assuming that sodium bromide is the bromide from which the bromine is derived; actually there are also other bromides present.

Figure 151 gives a schematic representation of the process by which sea water is caused to yield bromine. The water is made slightly acid with sulfuric acid and then sprayed into towers containing chlorine. The chlorine replaces the bromine in the bromides, thus forming elemental bromine. The liberated bromine is blown out of the water by a jet of air and absorbed in a sodium carbonate solution. The sodium carbonate converts the bromine to sodium bromide and sodium bromate, in which form it is stored. When bromine is desired, the bromide-bromate solution is acidified with sulfuric acid.



The bromine is removed by steam and subsequently separated by condensation.

Over 100 million tons of ocean water has been treated in a year by one plant alone, and a total of more than 100 million pounds of bromine has been produced in a single year. Bromine is used chiefly for the production of *ethylene dibromide*, $\text{C}_2\text{H}_4\text{Br}_2$, which is used in high-octane gasoline and as a soil fumigant (Chapter 31). Every gallon of gasoline requires the treatment of 20 gallons of sea water to obtain the necessary bromine. Other organic and inorganic compounds are also made from

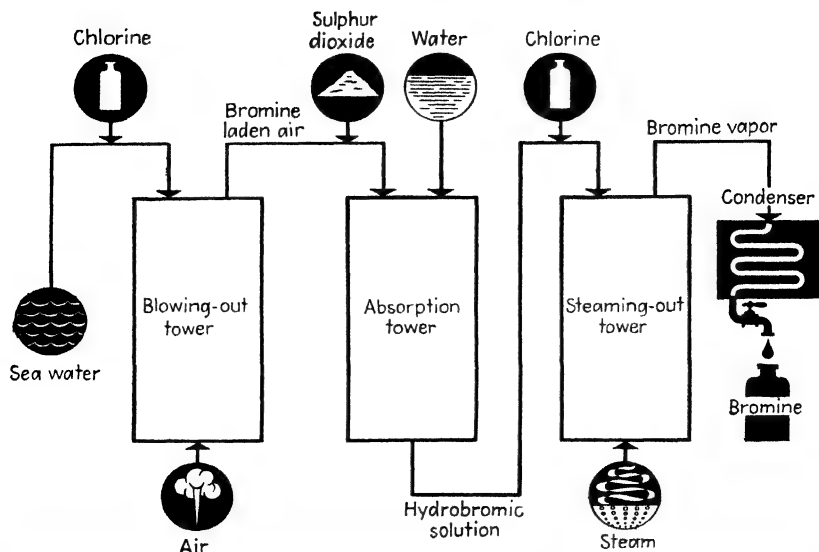


Figure 151. Bromine from sea water. (Courtesy of The Dow Chemical Company.)

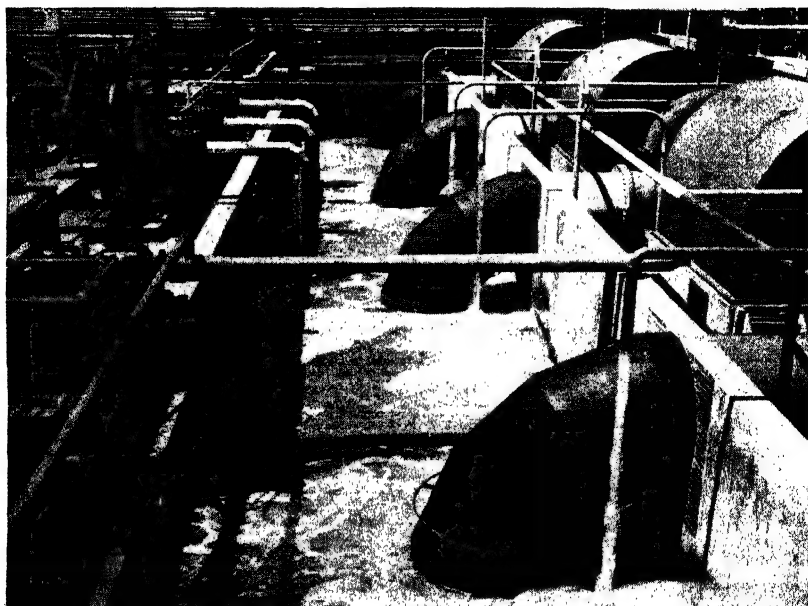


Figure 152. These pumps take in 230,000 gallons of sea water per minute from which bromine is obtained. (Courtesy of The Dow Chemical Company.)

bromine; notable among these is *silver bromide*, AgBr , used in photography. *Hydrogen bromide*, HBr , has little industrial importance.

Iodine. Iodine in the form of its compounds occurs in the ocean and particularly in seaweeds and kelp. It was discovered by accident in 1811, when Bernard Courtois was making saltpeter from seaweed. In cleaning out his plant equipment he added sulfuric acid to some

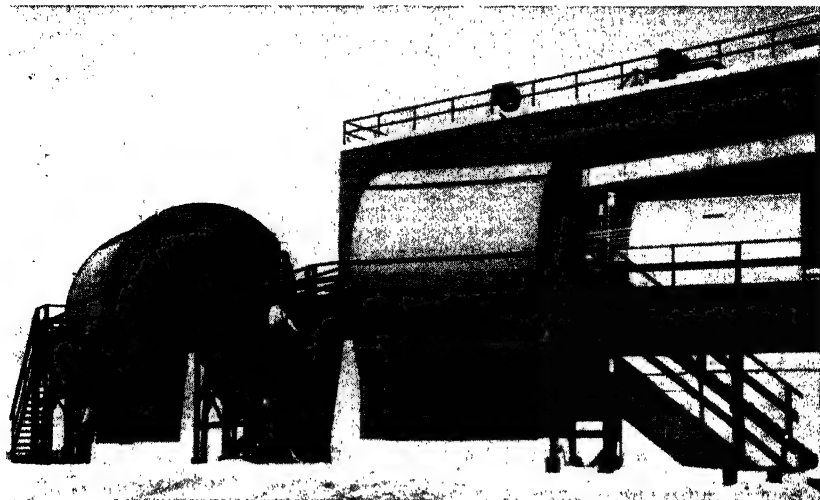


Figure 153. Two of the giant fans used to blow bromine out of treated sea water. (Courtesy of The Dow Chemical Company.)

residual salts and observed violet-colored vapors, which condensed to a solid iodine. For many years seaweed and kelp were the chief source of iodine, but later it was obtained from large deposits of sodium iodate, NaIO_3 , and sodium periodate, NaIO_4 , in Chile. At present most of the iodine used in the United States comes from iodides in certain oil-well brines.

Iodine is used in the synthesis of a number of organic dyes and drugs and in the preparation of silver iodide, AgI , used to some extent in photography. Sodium iodide is frequently added to salt (*iodized salt*) to ensure a sufficient amount of iodine in the diet. Iodine deficiency in the human body is largely responsible for cretinism and for the development of goiter.

The most familiar use of iodine is in the form of *tincture of iodine* used as an antiseptic. This consists of a solution of iodine and potas-

sium iodide in alcohol and is one of the most effective antiseptics known.

Hydrogen iodide is not used industrially to any appreciable extent.

EXERCISES

1. *New terms*: allotropic forms, flowers of sulfur, fixation of nitrogen, iodized salt, brimstone, contact process, nitrogen cycle, tincture of iodine, Frasch process, lead-chamber process, Haber process, bleaching powder.
2. What process should be used to make sulfuric acid from the sulfur dioxide recovered as a by-product of the metallurgy of copper? Explain.
3. Name three solid non-metallic elements; one liquid non-metallic element.
4. Outline the production of sulfur by the Frasch process. Upon what physical property of sulfur does this process depend?
5. Write equations for the reactions involved in the production of sulfuric acid from sulfur.
6. Write equations for the preparation of the following substances: (a) carbon disulfide, (b) pure nitrogen, (c) ammonia (a laboratory method), (d) bromine, (e) phosphorus.
7. Draw a picture of a "strike-anywhere" match, and indicate the chemicals located in the various portions of the match.
8. Write equations for two reactions associated with the etching of glass with hydrofluoric acid.
9. Name seven non-metals that occur uncombined in nature.
10. List the halogens in the increasing order of their color intensity.
11. What are three important uses of sulfur?
12. What are two ways in which sulfuric acid produced by the contact process differs from the sulfuric acid produced by the lead-chamber process?
13. What are two of the most important uses for nitric acid?
14. What is the relationship of fluorine to the atomic bomb?
15. What is *tincture of iodine*, and for what is it used?
16. Name three elements that exist in different allotropic forms.

17. Characterize non-metals as to their chemical properties and electronic configuration.
18. Explain why sulfuric acid production can be used as an indication of national prosperity.
19. What is the *nitrogen cycle*, and of what significance is it?
20. What is the chief difference between red and white phosphorus, other than color?
21. How did hydrogen fluoride help win World War II?
22. Write equations for the reaction between sodium bromide and chlorine in a manner similar to that used for the reactions which take place during electrolysis.
23. Approximately how many tons of chlorine are used yearly for the production of chlorine-containing organic compounds?

COLLATERAL READING

ELDER, SCOTT, and KANDA: "Textbook of Chemistry," Harper & Brothers, New York, 1948, Chapters 22, 23, 24, and 25.

HOLMES: "Introductory College Chemistry," The Macmillan Company, New York, 1946, Chapters XVI, XVII, XVIII, XXIII, XXIV, XXIX, XXX, XXXI, and XXXII.

RICHARDSON and SCARLETT: "General College Chemistry," Henry Holt and Company, Inc., New York, 1947, Chapters 18, 19, 24, 25, 27, 28, and 29.

SCHOCH, FELSING, and WATT: "General Chemistry," McGraw-Hill Book Company, Inc., New York, 1946, Chapters XXVIII, XXIX, XXX, and XXXI.

Carbon and Inorganic Carbon Compounds

THE TERM unique is ascribed to many things, usually after little thought and frequently with less accuracy. Carbon, however, is one of the truly unique substances of nature. It is an element that exists in allotropic forms as widely divergent as diamond and graphite—essentially the hardest and softest solids known. Carbon forms hundreds of thousands of compounds, while all of the other elements account for only about fifty thousand different compounds. In price, carbon in its various forms ranges from less than a cent to nearly \$3,000,000 a pound. It is with us in sickness and in health in the form of medicinals and food; and when we die, we are buried in a pine box—made up of carbon compounds.

The remainder of this book will be devoted largely to this fascinating element and its compounds.

The Allotropic Forms of Carbon. Pure carbon is found in two crystalline forms, diamond and graphite, and in a number of amorphous and semi-amorphous forms such as coke, charcoal, carbon black, and lampblack.

Diamonds have interested man since Biblical times because of their properties of brilliance, hardness, and scarcity. They have been used to ward off insanity, inactivate poisons, counteract the evil eye, and serve as the peacemaker between man and wife. To the chemist, diamonds are of interest because they represent a form of carbon that is the hardest known naturally occurring substance and are very resistant to chemical action. The density of diamond is 3.5, and it melts at 3500°C.

Usually diamonds are dark brown or black in color. Such diamonds are used in industry for polishing and glass cutting and in the con-

struction of the cutting edges of rock drills, rock-cutting saws, etc. These diamonds are called *borts*.

Less frequently but more familiarly, diamonds are clear and colorless. These are the gem stones of incomparable beauty and brilliance. This brilliance is caused by diamond's high index of refraction, its density, and the method of cutting. Occasionally diamonds are tinted blue, green, or red.

The weight of diamonds and other gem stones is given in terms of *carats*. A carat is equal to 0.200 gram; the word is derived from the Greek word meaning "carob bean." Presumably the carob bean was remarkably uniform in weight and was used as a counterbalance by the Greeks in weighing gems. One of the largest diamonds ever found was the Cullinan diamond (Fig. 154), which weighed 3024 carats. The price per carat of perfect diamonds is about \$1200.

Diamonds are found in appreciable quantities in South Africa and in Brazil and less extensively in Arkansas. Innumerable attempts have been made to synthesize diamonds, but they have all met with indifferent success. Tiny diamonds have been synthesized, but the cost was always many times their value.

Graphite, the other form of crystalline carbon, is similar to diamond in its lack of chemical activity and in its melting point. In contrast to diamond, however, graphite has a lower density (2.25) and is black and opaque, soft, and a good conductor of electricity. These differences in physical properties are caused by a difference in crystalline structure.

Graphite is found in nature in large quantities in Ceylon, Siberia, Austria, and Madagascar and in lesser amounts in the United States, Canada, and Mexico. It is produced artificially by the *Acheson process*, which consists in heating amorphous carbon in an electric furnace at about 4000°C. At this temperature the carbon volatilizes and then condenses in a cooler portion of the furnace in the form of crystalline graphite.

Graphite is used in the manufacture of electrodes for high-temperature furnaces such as those employed in the production of magnesium and aluminum. It is also utilized as a pigment, in the manufacture of "lead" pencils, and as a high-pressure and -temperature lubricant.

Following are some of the amorphous or semi-amorphous forms of carbon.

Wood charcoal is produced by the heating of wood, nutshells, or similar material in the absence of air, a process called *destructive distillation*. In addition to charcoal, there is produced a number of organic chemicals as by-products, and the charcoal industry at one time was an

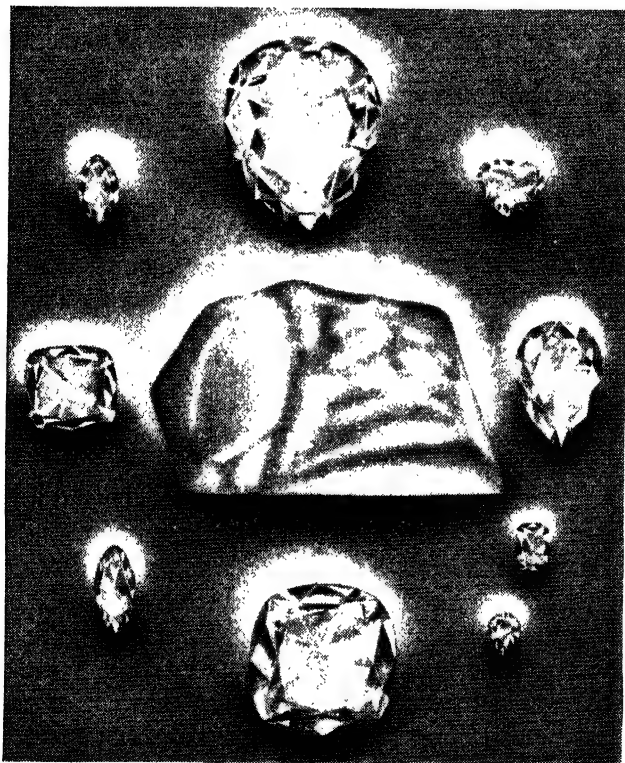


Figure 154. The Cullinan diamond and some crown jewels of England which were cut from it. Illustration about $\frac{1}{3}$ actual size. (Courtesy of the Arthur A. Crafts Co., Inc.)

important source of these chemicals. At present all of them can be produced more efficiently from petroleum or air, coal, and water.

Good charcoal is deep black in color and breaks with a bright fracture; it rings when struck. Charcoal is used as a fuel because it is essentially pure carbon and consequently burns without smoke. It is also employed in the manufacture of gunpowder and by the iron and steel industry. A special charcoal made from coconut shells has the

ability to adsorb large amounts of certain gases, and thus it is utilized in gas masks to remove poisonous gases from the air. It is also employed in industry to recover volatile solvents used in painting manufactured objects. This type of charcoal is called *activated carbon* or *activated charcoal*.

Bone black is produced as a result of heating "green" bones and consists of about 10 per cent finely divided carbon and the rest mainly calcium phosphate. The carbon has the ability to adsorb large colored molecules, and bone black is used for the decolorization of many colored and turbid solutions, especially sugar sirups in the preparation of table sugar.

Lampblack is relatively pure and very finely divided carbon produced by burning light oil in a limited amount of air. It is employed in the preparation of inks, paints, stove polish, crayons, carbon paper, etc.

Carbon black is also nearly pure carbon produced by the incomplete combustion of natural gas. About 7 pounds of carbon is obtained from 100 pounds of natural gas in the most efficiently operated plants. Ninety-five per cent of the carbon black produced is utilized in the manufacture of rubber tires; each automobile tire contains 20 to 40 per cent carbon, the amount depending upon the type of rubber used. The wearing surface of the tire is actually the particles of carbon in the rubber. The other uses of carbon black are similar to those of lampblack.

Coke has been cited as an essential in the metallurgy of a number of metals, especially in the production of pig iron. Coke is formed when bituminous coal is heated in the absence of air; the apparatus used is depicted schematically in Fig. 155. This distillation of coal not only furnishes coke but also produces a wide variety of chemicals as by-products. These chemicals are used extensively by the chemical industries for the production of many commodities. Chapter 28 is concerned in detail with these important chemicals.

Coke is also employed as a fuel in industry and to a small extent in the home. As a fuel it has the advantage over coal and wood in that coke gives a "clean" flame and only a small amount of ash.

Binary Compounds of Carbon. The inorganic compounds of carbon containing more than two different elements have been mentioned in Chapter 16. The most important compounds of this type are the carbonates.

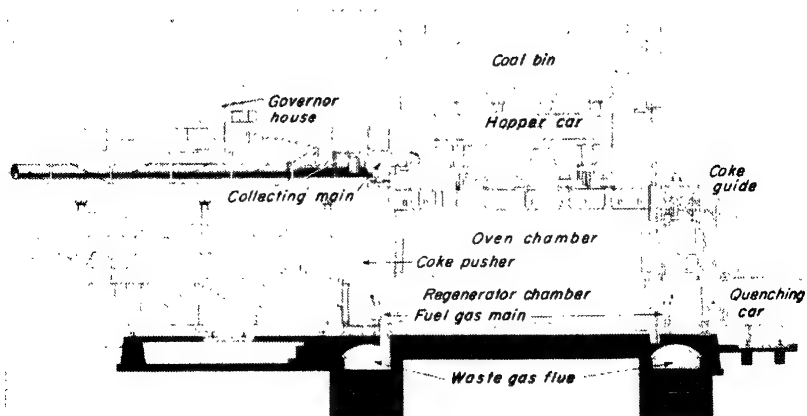


Figure 155. Schematic drawing of a coke oven. (Courtesy of the Bethlehem Steel Co.)

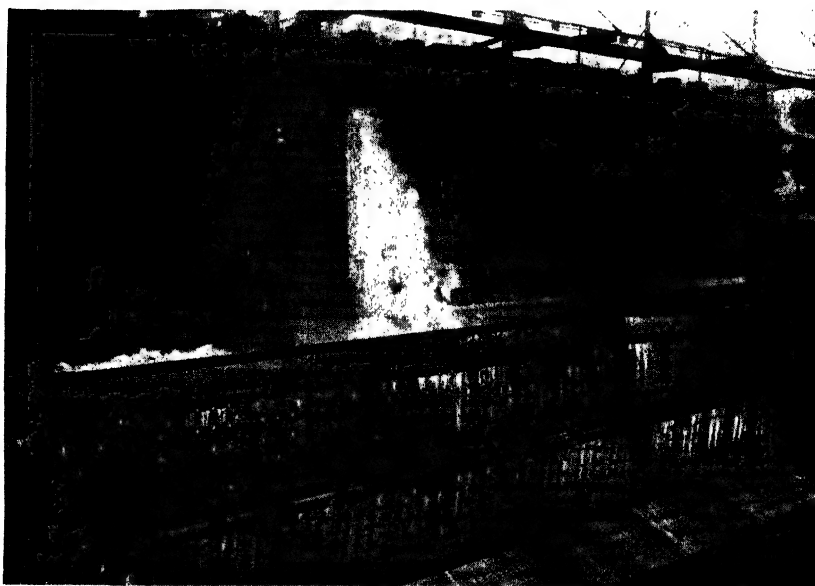


Figure 156. Coke being pushed from a coke oven into a quenching car. (Courtesy of the Bethlehem Steel Co.)

There are several binary compounds of carbon that are widely used both in industry and in the home. Some of these are considered organic compounds because of their properties and will be discussed later. The few binary compounds of carbon that are predominantly inorganic in nature will be described in this chapter. One of them, carbon disulfide, has been included in Chapter 22.

Carbon monoxide, CO , is a colorless, odorless, tasteless, non-irritating but highly toxic gas that is formed by the incomplete combustion of nearly all carbonaceous substances such as gasoline, fuel oil, wood, coke, coal, and natural gas.

Carbon monoxide has a greater affinity for hemoglobin (the oxygen carrier in the blood) than has oxygen; thus when there are even traces of carbon monoxide in the air, the hemoglobin reacts with it in preference to the oxygen. As the hemoglobin progressively becomes more and more saturated with carbon monoxide, the blood loses its ability to

carry oxygen and one dies from internal suffocation. Figure 157 gives an indication of the relation between carbon monoxide concentration in the air, length of exposure, and physiological action.

This discussion of the lethal properties of carbon monoxide is not just of academic interest but of very real concern to everyone, for essentially all heating is done directly or indirectly as a result of the burning of carbonaceous materials. Each year many lives are lost by carbon monoxide poisoning resulting from the inefficient burning of natural gas in home heating units, from allowing automobile engines to run in closed garages, and from faulty flues. Most burning fuels produce at least a small amount of carbon monoxide; the exhaust gas of an automobile on a cold morning contains 7 to 12 per cent carbon monoxide.

Carbon monoxide gives no warning, and the symptoms of carbon monoxide poisoning are, unfortunately, those which might afflict any-

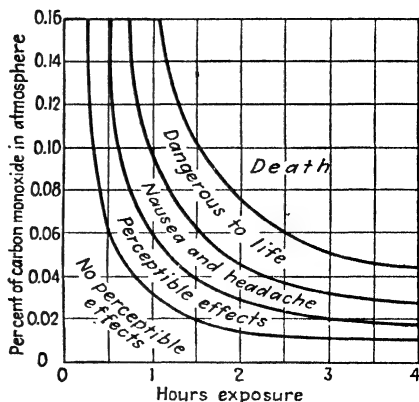
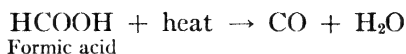


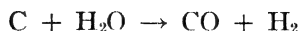
Figure 157. Effects of carbon monoxide for a given period of time on human beings. [*Journal of Chemical Education* **25**, 343 (1948).]

one at any time, namely, headache, mental dullness, and physical inertia. There is no acquired or natural immunity to the gas; repeated exposure produces the same effects each time.

In spite of the poisonous character of carbon monoxide it is used extensively in industry both in the metallurgy of iron and other metals and in the synthesis of several organic compounds. It is prepared in the laboratory by the decomposition of formic acid.



Industrially, either carbon monoxide is prepared as it is used, for example, in the metallurgy of iron, or it is prepared by passing steam over coke.



This mixture of CO and H₂ is called *water gas* and is used as a fuel, as a source of carbon monoxide, and as a source of hydrogen (Chapter 10).

Carbon dioxide, CO₂, is also a colorless, odorless, and tasteless gas, but it is non-toxic in the usual meaning of the word. It can be deadly, but only by excluding oxygen, with death resulting from suffocation.

Carbon dioxide is a major article of commerce but one that is infrequently produced as the main product of a reaction. Found in nature in commercial quantities only in a few gas wells, it is a by-product of a number of chemical processes, and these are its chief sources. Carbon dioxide produced by the combustion of coal and coke is recovered by passing the gases into a solution of sodium carbonate, wherein the following reaction takes place:

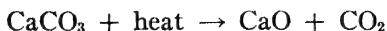


The sodium bicarbonate is heated to liberate the carbon dioxide.

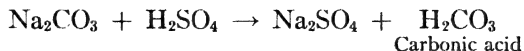


The sodium carbonate is regenerated and may be used again.

Carbon dioxide is also a by-product of the production of lime,



and the fermentation of various materials to produce alcohol. In the laboratory, carbon dioxide is produced conveniently by the action of an acid on a carbonate.



Carbonic acid is unstable and decomposes to carbon dioxide and water.



The use of carbon dioxide in the production of sodium carbonate and sodium bicarbonate has been mentioned in Chapter 16. It is also employed in the production of certain lead compounds used in paints and in the synthesis of certain types of organic compounds.

Carbon dioxide is used in carbonated beverages, which are produced by dissolving carbon dioxide in flavored water under a pressure of 60 to 120 pounds per square inch. At these pressures carbon dioxide is appreciably soluble in water. Joseph Priestley is credited with being the founder of the carbonated-beverage industry—in the minds of some an achievement more noteworthy than his work with oxygen.

When liquid carbon dioxide is permitted to evaporate rapidly, it is cooled to such an extent that some of the carbon dioxide becomes a snow-like solid. Compressed blocks of this carbon dioxide snow are called *dry ice*. Dry ice vaporizes directly to a gas at -78.7°C ., leaving no liquid residue; because of this property and its low temperature, it is employed extensively as a refrigerant.

Because carbon dioxide will not support combustion and is heavier than air, it is used extensively as a *fire extinguisher*. There are several types of apparatus, or “fire extinguishers,” for dispensing the carbon dioxide. A common type is simply a cylinder of liquid carbon dioxide fitted with an easily opened valve. Another, more complicated type is illustrated in Fig. 158. When this type is inverted, the stopper *A* falls from bottle *B*, which contains sulfuric acid. The acid mixes with the sodium carbonate (or bicarbonate) solution, and carbon dioxide is produced. The gas developed within the apparatus forces the mixture out through nozzle *C*. Aluminum sulfate is usually added to the sulfuric acid, and licorice or similar material is added to the sodium carbonate solution. This combination causes the solution and carbon

dioxide to issue from the nozzle as a foam that blankets the burning object, and both the water and the carbon dioxide contribute toward putting out the fire. The Foamite fire extinguisher is one of this type.

Carbon dioxide fire extinguishers are useful only for small fires and for oil fires, which cannot be put out by a stream of water. Oil fires are

frequently extinguished by a blanket of steam that serves to replace air, as does carbon dioxide.

Fire extinguishers that contain heavy non-flammable fluids other than water are also used on small fires. The compound usually contained in these fire extinguishers (Pyrene) is carbon tetrachloride, CCl_4 , a non-flammable organic compound. These fire extinguishers also function by blanketing the flaming material, thus excluding oxygen and smothering the flame.

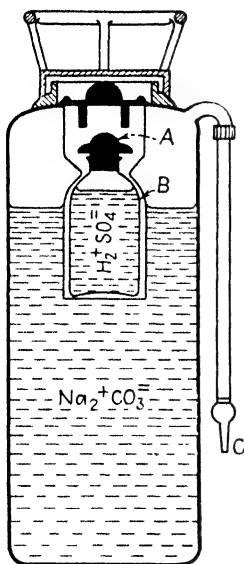
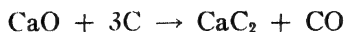


Figure 158. Fire extinguisher.

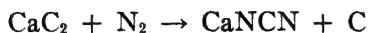
Carbon dioxide enters into a cycle in nature similar to that of nitrogen. The *carbon cycle* consists in plants taking in carbon dioxide, which is changed in the green leaves to carbohydrates and oxygen. The oxygen is exhaled by the leaves, and the carbohydrates are used to build the fibrous portion of the plant. When the plants are eaten by animals, the carbohydrates are oxidized to carbon dioxide by the inhaled oxygen and the heat produced in the oxidation keeps

the body warm. The carbon dioxide is exhaled and thus is available to repeat the cycle. The carbon-carbon dioxide cycle accounts for the relatively constant amount of carbon dioxide in the atmosphere.

Calcium carbide, CaC_2 , is made by heating lime and coke in an electric furnace at 2800 to 2900°C.



The operation is a continuous one, with the molten calcium carbide being drawn off and cooled to a dense gray solid. Calcium carbide is used in the preparation of acetylene, a very important organic compound, and in the manufacture of *calcium cyanamide*,



which in turn is used as a fertilizer and in the production of ammonia and sodium cyanide, NaCN.

Silicon carbide, SiC, which is usually called by the trade name *Carborundum*, is produced in an electric furnace (Fig. 159) from a mixture of coke, sawdust, sand, and salt.

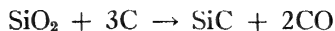


Figure 159. Loaded carborundum furnace. (Courtesy "The Carbo Wheel," The Carborundum Company.)

A cross section of such a furnace is shown in Fig. 160. The sawdust and salt do not enter directly into the reaction, but the former is present to make the mixture more porous, and the latter makes the mass a better conductor of electricity.

Silicon carbide appears in the form of sharp, iridescent crystals that are extremely inactive chemically and almost as hard as diamond. Owing to the hardness of these crystals, they are used as an *abrasive* in the manufacture of grinding stones and wheels, polishing papers and cloths, cutting wheels, etc. The use of abrasives has also made possible

the mass production of precision parts for airplane engines and similar pieces of equipment.

To make a grinding or cutting wheel, silicon carbide is broken up; sorted to size; and then mixed with clay and another binder such as a phenolic resin, shellac, or rubber; and then baked. The sharp crystals of silicon carbide constitute the cutting or grinding portion of the

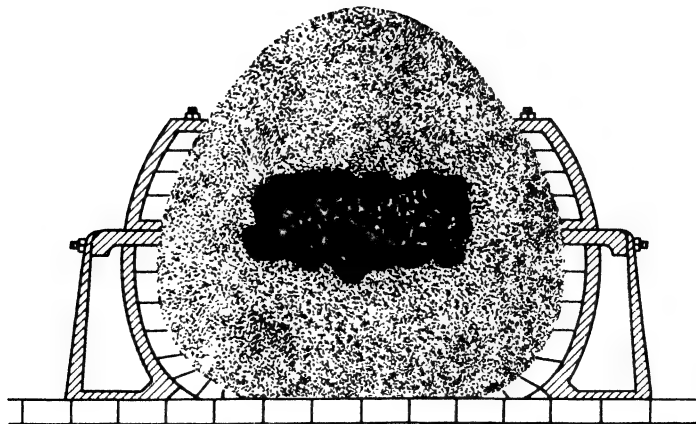


Figure 160. Cross section of a carborundum furnace. The center is pure carbon. (Courtesy of The Carborundum Company.)

wheel, which is used for cutting rods and other metal forms with great speed.

Other compounds besides silicon carbide are also used for grinding, cutting, and polishing, each having some particular use for which it is most suited. The following list is in decreasing order of hardness of the materials.

Diamond (C)	Quartz (sand— SiO_2)
Silicon carbide (SiC)	Iron and steel grit (Fe)
Aluminum oxide (Al_2O_3)	Pumice (silicates)
Garnet crystals (complex silicate)	Rouge (Fe_2O_3)

Of the naturally occurring materials, the aluminum oxide mineral *corundum* is next in hardness to the diamond. Made synthetically, it goes by various trade names such as Alundum and Aloxide; it is used

in a manner similar to silicon carbide. An impure form of corundum is called *emery* and is used to make emery cloth and emery wheels.

GEM STONES

The term *gem* is used in its widest sense to include all minerals that by reason of their beauty, brilliance, hardness, and rarity are valuable for personal adornment. In a more restricted sense the term is applied to precious stones after they have been cut and polished as jewels, the minerals being called *gem stones*. Gems are further divided into the *precious stones*, diamond, ruby, sapphire, and emerald, and the *semi-precious stones*, which include opal, topaz, aquamarine, zircon, amethyst, garnet, spinel, and many others. *Pearls* are sometimes classified as precious stones, but they are usually considered to be in a class by themselves.

Hardness is an essential property of a gem stone, for it permits the gem to take a high polish and to withstand the abrasion resulting from normal exposure to sand and grit. No matter how beautiful a stone may be, it is useless unless it can take and keep a polish. The Mohs scale of hardness has been mentioned elsewhere (Chapter 9). As a general rule a gem stone will not wear well if its hardness is equal to or less than that of quartz, because dust and dirt contain an appreciable amount of sand (quartz). Even zircons, which are slightly harder than quartz, will become scratched and dulled in a relatively short time. A steel file will scratch anything with a hardness less than 7 (quartz).

The beauty and value of many gems depend on the depth or absence of color. With the colored stones the value is related to their transparency and depth of shade. The color is usually imparted to the gem by traces (sometimes very minute traces) of impurities. For example, aluminum oxide is colorless, but its impurities produce red rubies, blue sapphires, and other shades. The colors of gem stones are frequently fugitive and fade in sunlight. Exposure to heat also often alters colors, sometimes resulting in an improvement in the value of the gem. Yellow topaz when heated turns to a beautiful pink; brown zircons change to blue, probably because of a change in the valence of iron in an iron compound present as an impurity.

The *brilliance* of a gem is determined by its refractive index, density,

and method of cutting. Diamond is in a class by itself, although colorless zircon approaches it in brilliance.

The *price* per carat of precious and especially semi-precious stones varies widely depending upon such factors as size, color, cut, and demand. The only gem with a stable price is diamond, and this is an induced stability. In general, emeralds and natural rubies are more



Figure 162. Natural and synthetic star sapphires. The smaller stone is the synthetic sapphire. (Courtesy of The Linde Air Products Company.)

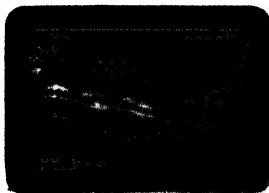
expensive than diamonds. Many semi-precious gems may be purchased at \$5 to \$10 a carat.

Many superstitions have developed around specific diamonds and certain other gem stones. The emerald is supposed to benefit the eyes and amethysts to prevent drunkenness; opals are believed by some to bring bad luck.

Table 9 contains a list of the more common of the precious and semiprecious gem stones, together with their chemical composition and other pertinent data. A number of these gem stones are shown in Fig. 161.

Synthetic Gems. Attention has already been called to attempts to make synthetic diamonds. More success has been achieved in synthesizing the aluminum oxide gems.

Synthetic rubies and sapphires are made in large numbers by melting aluminum oxide in an oxyhydrogen flame in the presence of a



Beryl
(Diamantina, Brazil)



Diamond
(Murfreesboro, Ark)



Emerald
(Bom Jesus dos Meiras, Brazil)



Aquamarine
(Marambaia, Brazil)



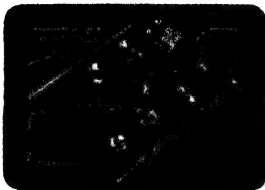
Ruby on calcite
(Burma)



Opal
(Australia)



Amethyst



Topaz
(Brazil)



Chrysoberyl
(Minas Geraes, Brazil)

Figure 161 Gem stones

suitable impurity to impart the desired color. These synthetic gems have the same chemical, physical, and optical properties as the natural gems, and even an expert finds it difficult to distinguish the one from the other. A recent advance has been the synthesis of star rubies and sapphires that are even superior to those found in nature (Fig. 162).

Synthetic sapphires and rubies are employed for jewel bearings in

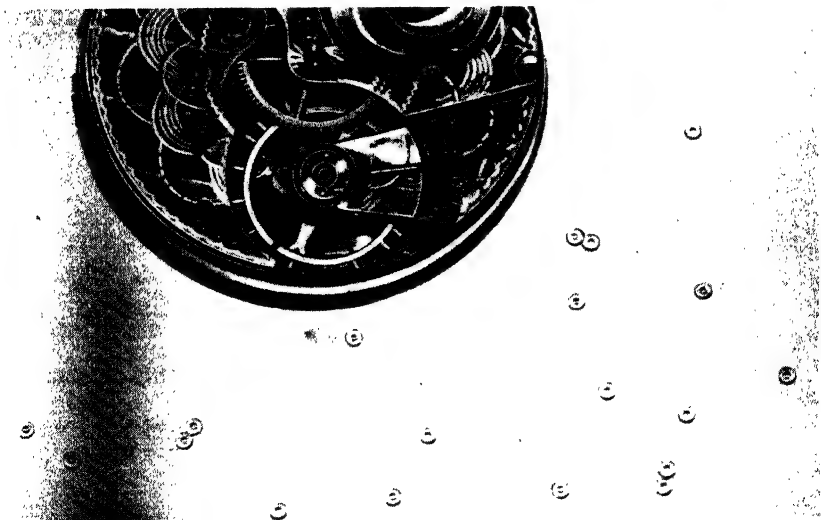


Figure 163. Synthetic sapphire and ruby watch bearings. (Courtesy of The Linde Air Products Company.)

watches and other precision instruments, extrusion dies, cutting and burnishing tools, knife-edges, and many other uses that require a very hard and smooth material.

The only other gem stone synthesized in quantity is spinel, a mixture of magnesium oxide and aluminum oxide. Its uses parallel those of the aluminum oxides. The other semi-precious stones are too inexpensive to warrant synthesis. The emerald is too complex in structure.

TABLE 9. Gem Stones

Name	Chemical composition	Color	Transparency	Hardness†	Source
<i>Silicon dioxides (quartz):</i>					
Agate (onyx, sardonyx, etc.)	SiO ₂	Variety of colors	Semi-transparent to opaque	6.5	Brazil, United States, India
Amethyst	SiO ₂	Pale violet to dark plum	Clear	7.0	Russia, Brazil, Uruguay
Bloodstone . . .	SiO ₂	Dark green with red jasper spots	Opaque	6.5	
Citrine	SiO ₂	Yellow	Clear	7.0	Brazil
Opal	SiO ₂ , 6-10% H ₂ O	White, black, blue, gray, yellow to orange-red	Translucent	5.5-6.0	Australia, Hungary, Mexico
Quartz (rock crystal)	SiO ₂	Colorless	Clear	7.0	Widely distributed
Spanish topaz (citrine)	SiO ₂	Dark yellow, brown	Clear	7.0	Brazil
<i>Aluminum oxides (corundums):</i>					
Ruby*	Al ₂ O ₃	Red	Clear	9.0	Upper Burma, Siam, Ceylon
Sapphire*	Al ₂ O ₃	Blue	Clear	9.0	Ceylon, Siam, Montana
Oriental topaz	Al ₂ O ₃	Yellow	Clear	9.0	Ceylon, Burma, Siam
<i>Carbon:</i>					
Diamond*	C	Colorless, yellow, pink, blue, brown, black	Clear	10.0	Africa, Brazil, Arkansas
<i>Calcium carbonates:</i>					
Coral	CaCO ₃	Bright pink to dark red	Opaque	5	Mediterranean Sea
Pearls*	CaCO ₃	Translucent white, pink, black	Opaque	...	Persian Gulf, Australia, South Seas
<i>Silicates:</i>					
Zircon	ZrSiO ₃	Colorless, variety of colors	Clear	7.5	Ceylon, Siam, Australia

<i>Name</i>	<i>Chemical composition</i>	<i>Color</i>	<i>Trans- parency</i>	<i>Hard- ness</i>	<i>Source</i>
Topaz	$(\text{AlF})_2\text{SiO}_4$	Colorless, yellow, brown, pink, blue	Clear	8.0	Brazil, Ceylon, Rus- sia, California
Aquamarine (emerald) . . .	$\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$	Pale blue to sea green	Clear	7.5	Russia
Emerald*	$\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$	Green	Clear	7.5-8.0	Colombia, Russia
Garnet	$\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	Deep red, var- iety of col- ors	Clear	6.5-7.5	Czechoslovakia, Arizona, Utah
Pyrope	$\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$				
Almandine . . .					
Jade					
Jadeite	$\text{NaAlSi}_2\text{O}_6$	White to	Semi-trans- parent to	6.5-7.0	Upper Burma, New Zealand, Siberia
Nephrite	$\text{CaMg}_3\text{Si}_4\text{O}_{12}$	green	opaque		
Lapis lazuli . .	$\text{Na}_4\text{Al}_3\text{S}_3\text{Si}_3\text{O}_{12}$	Azure-blue	Opaque	5.5-6.0	Siberia, Chile, Af- ghanistan
<i>Aluminates:</i>					
Alexandrite . .	BeAl_2O_4	Green (day- light), red (artificial light)	Opaque	8.5	Ural Mountains, Cey- lon
Chrysoberyl . .	BeAl_2O_4	Yellow, pale green, brown	Clear	8.5	Brazil, Ceylon, South Africa
Peridot	BeAl_2O_4	Yellow-green	Clear	6-7	Brazil, Ceylon
Spinel	MgAl_2O_4	Rose, red, blue	Clear	8.0	Burma, Siam, Ceylon
<i>Complex:</i>					
Tourmaline . .	Complex	Great variety of colors	Opaque	7.5	California, Russia, Brazil
Turquoise . . .	Complex	Light blue	Opaque	6	Sinai Peninsula, New Mexico

* Classed as precious stones. Most of the others are classed as semi-precious stones.

† The Mohs scale of hardness.

EXERCISES

1. *New terms:* carat, destructive distillation, water gas, carbon cycle, gem, precious stones, synthetic gems, Acheson process, activated carbon, dry ice, abrasive, gem stones, semi-precious stones, borts.
2. Account for the relatively constant amount of carbon dioxide in the atmosphere in view of the fact that animals are constantly replacing the oxygen of the atmosphere with carbon dioxide.
3. List four ways in which carbon differs from other elements.

4. What are the two physical properties of diamond that cause it to be a gem of incomparable worth?
5. Characterize a good charcoal.
6. Why is carbon monoxide an insidious compound?
7. Write equations representing the following indicated reactions:
 - a. Preparation of carbon monoxide from formic acid
 - b. Preparation of calcium carbide
 - c. Preparation of calcium cyanamide
 - d. Preparation of silicon carbide
8. Write equations for the reactions involved in the recovery of carbon dioxide from the gaseous products of the combustion of coke.
9. Name three synthetic gems, and tell in what way each differs from the corresponding naturally occurring gem.
10. Name three compounds whose production yields carbon dioxide as a by-product.
11. Name two crystalline and five amorphous forms of carbon.
12. Give an important use of graphite. Upon what property of graphite is this use dependent?
13. What is the largest single use of coke?
14. List five possible sources of carbon monoxide that could endanger human life.
15. List in the order of their decreasing hardness five different substances used as abrasives.
16. Name four precious and seven semi-precious gem stones.
17. What is meant by the statement that the stability of the price of diamonds is an "induced stability"?
18. Assuming the Cullinan diamond was one of perfect quality, how many dollars was it worth before cutting? For the sake of this problem assume that an uncut diamond is worth half as much per carat as a cut diamond.
19. What would be a person's condition who had been in an atmosphere containing 0.05 per cent carbon monoxide for one and one-half hours?

COLLATERAL READING

ELDER, SCOTT, and KANDA: "Textbook of Chemistry," Harper & Brothers, New York, 1948, Chapter 39.

HOLMES: "Introductory College Chemistry," The Macmillan Company, New York, 1946, Chapter XII.

RICHARDSON and SCARLETT: "General College Chemistry," Henry Holt and Company, Inc., New York, 1947, Chapters 30 and 31.

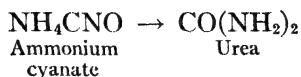
SCHOCH, FELSING, and WATT: "General Chemistry," McGraw-Hill Book Company, Inc., 1946, Chapters XXVIII and XXIX.

Carbon in Organic Compounds. Hydrocarbons

FOR MANY years chemistry has been divided rather arbitrarily into a study of organic compounds and a study of inorganic compounds. The preceding chapters have been devoted to inorganic compounds and to some of the natural laws that describe their behavior. In the remaining chapters we shall study those compounds classified as organic; these usually have complex structures, and all of them contain the element carbon. It should be noted, however, that the natural laws studied in connection with inorganic compounds apply equally to organic compounds.

The term *organic* originated with the belief that compounds of this type were always associated with living (organic) matter. In fact, until the nineteenth century this classification had no basis in chemical composition. A consequence of this philosophy was the belief that inorganic compounds could not be changed into organic compounds without the intervention of a "vital principle." This was a period of little progress in the study of organic chemistry.

In 1828 Friedrich Wöhler (Fig. 164) performed an experiment in the back room of his chemist's (apothecary's) shop that is considered by many as the first experiment in modern organic chemistry. The experiment was the simple one of heating ammonium cyanate and producing urea.



Until this time ammonium cyanate was classified as an inorganic compound (as it still is) and urea was an organic compound (as it still is), and that was that. Chemists believed that because urea had always

come only from a living source that it always would. Wöhler repeated the experiment many times before he had the courage to report that he had changed an inorganic compound into an organic compound. The impact of his discovery can hardly be appreciated today because we are frequently reminded that many organic compounds come from "limestone, coal, and water." The ensuing attempts to prove Wöhler wrong led to the synthesis of many new and useful organic compounds from inorganic compounds and ultimately resulted in the development of modern organic chemistry.

There is at present no sharp line of demarcation between organic chemistry and inorganic chemistry. The following definition of organic chemistry, although inadequate in some respects, will prove useful: *Organic chemistry is the chemistry of the hydrogen compounds of carbon, and their derivatives.* These derivatives may contain one or more of the following elements: oxygen, nitrogen, sulfur, the halogens, and occasionally others.

Delimitation of organic chemistry to the hydrogen compounds of carbon and their derivatives may seem unduly restrictive until it is realized that there are known over 500,000 organic compounds with more being synthesized every day. These compounds are everywhere—in our food and drink, in our medicines, insecticides, plastics, fuels, clothing, houses, etc., in all living matter. Although inorganic compounds are as widely distributed there are only about 50,000 known inorganic compounds. Industrially, a few inorganic compounds are produced in huge quantities at a low cost, while appreciably more organic compounds are produced in smaller amounts at a higher cost.

Carbon in Organic Compounds. A systematic study of a branch of chemistry dealing with so large a number of compounds may seem

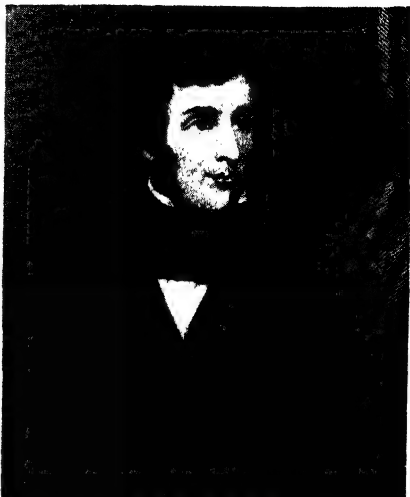
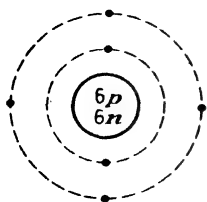


Figure 164. Friedrich Wöhler. (Courtesy of The Edgar Fahs Smith Memorial Collection in the History of Chemistry, The University of Pennsylvania.)

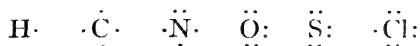
little short of impossible. It would be if it were not for the fact that carbon is, after all, an element and as such its atoms follow the same behavior patterns as the elements already studied. Carbon atoms, in common with all atoms, react in such a way as to obtain a stable con-



figuration of eight electrons in their outer shell, and their electrons always go around in pairs (rule of two). Carbon differs mainly in the manner in which it usually acquires an outer shell of eight electrons, and a review of its atomic structure (Chapter 5) will show why this must be so.

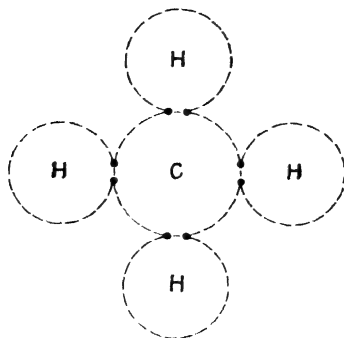
An understanding of the relationship between atomic structure and chemical reactivity will do much to remove the apparent mystery of organic chemistry.

An atom of carbon contains 6 protons and 6 neutrons in its nucleus with 2 electrons in its first shell and 4 electrons in its other shell. Because it is necessary for our purposes to consider only the electrons in the outer shell, it is convenient to let the symbol of the atom represent all of it except those electrons, *i.e.*,



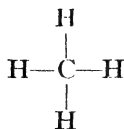
This method of representation is particularly useful in organic chemistry.

Single Bonds. For carbon to obtain a stable configuration by a transfer of electrons it would be necessary for it either to gain or to lose four electrons. A transfer of electrons of this magnitude would require a large amount of energy. Another possibility exists, however, and that is for carbon to gain at least partial stability by sharing electrons with other elements or with other carbon atoms. Hydrogen with its one electron has a strong affinity for another electron so that it may achieve the stable helium configuration ($\cdot\text{He}\cdot$). Hydrogen, however, does not have the ability to gain this electron from another atom as does chlorine, for example, but it does have the ability to share an electron from another atom in return for sharing its electron with the other atom. It would appear that carbon and hydrogen have much in common, and it is not surprising that they get together in a mutually satisfactory partnership; the result is the relatively stable compound **methane**, which has the following structure:



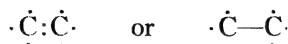
This compound is relatively stable because each atom in it has at least a share in enough electrons to give it a stable configuration. Compounds of this type will react only with a reagent that will form products with even greater stability. A basic law of nature is that all spontaneous changes which take place in the universe do so in such a way that greater stability is attained as a result.

It is customary in organic chemistry to represent each pair of electrons by a straight line called a *single bond*, and this permits one to write the formula for methane more simply.



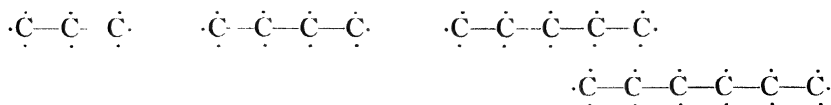
It should always be kept in mind that each bond represents two electrons and that in organic chemistry each carbon atom will always have four of these bonds.

In addition to having the ability to share an electron with hydrogen, carbon may also share its electrons with a number of other elements as well as with other carbon atoms. The union of two carbon atoms may be represented by either



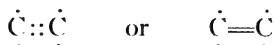
and the other electrons may be shared by other carbon atoms, hydrogen, or other elements. The sharing with other carbon atoms results

in long-chain carbon compounds in which the carbon atoms are joined by single bonds, for example,



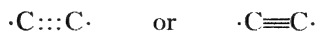
All of these compounds (with hydrogen atoms sharing the other electrons) are known, as are a great many similar ones.

Double Bonds. It is also possible for two pairs of electrons to be shared by two carbon atoms. The structure of the resulting union may be represented as follows:



and the carbon atoms are said to be joined by a *double bond*. The remaining electrons may be shared by various other elements, or carbon. A large number of different compounds of this type containing only carbon and hydrogen is thus possible.

Triple Bonds. Three electron pairs may be shared by two carbon atoms to give a type of union illustrated by



These are said to contain a *triple bond*. Only one simple compound of this type is of importance, and that is the one wherein the other electrons are shared with hydrogen, $\text{H}-\text{C}\equiv\text{C}-\text{H}$ (acetylene, C_2H_2).

The ability of carbon atoms to unite with other carbon atoms by forming single, double, and triple bonds accounts in considerable measure for the large number of organic compounds.

Comparison of Organic and Inorganic Compounds. The covalent nature of the bond between atoms in organic compounds endows them with both physical and chemical properties that are markedly different from the predominantly ionic inorganic compounds. Probably the most striking difference is in their rate of reaction. Because of the stability of the shared electron bond, organic compounds react slowly even at high temperatures; on the other hand, the rate of reaction of ionic compounds is very great even at room temperature. The nature

of the reactions involved is, of course, quite different, as will be shown in later chapters.

In addition to influencing the rate of reaction, the shared electron bond also modifies the physical properties of compounds. Organic compounds are non-electrolytes, relatively volatile, frequently liquids, and likely to be insoluble in water. In a general way, just the opposite is true of inorganic compounds. There are also many organic compounds having the same molecular formula but different structures and different physical and chemical properties. These compounds are called *isomers*, and this phenomenon will be discussed in more detail later in this chapter. Isomerism has been studied relatively little in the field of inorganic chemistry.

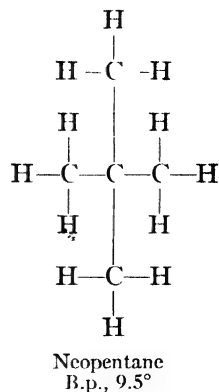
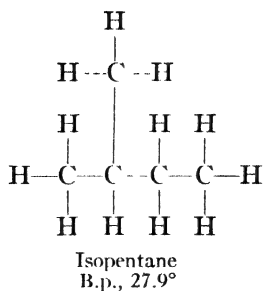
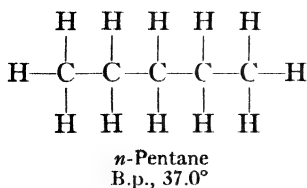
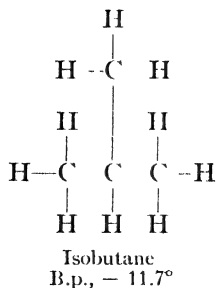
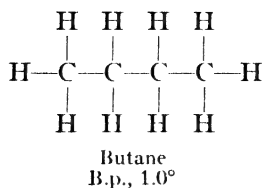
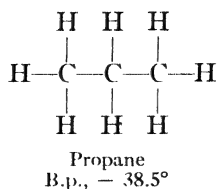
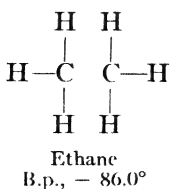
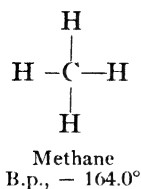
All of the foregoing statements are no more than broad generalization; many exceptions can be found in both organic and inorganic chemistry. Any attempt to generalize with respect to large numbers of chemical substances must necessarily involve many exceptions.

Hydrocarbons. From the preceding discussion it will be seen that there is actually and potentially a very large number of compounds containing only carbon and hydrogen. These hydrides of carbon are called *hydrocarbons*. They are the first organic compounds to be studied in detail because of their importance and simplicity and also because all other organic compounds may be considered as derived from them.

Paraffin Hydrocarbons. The structure of the simplest hydrocarbon, *methane*, CH_4 , has already been given in the discussion of carbon in organic compounds. Methane is the first member of a long series of hydrocarbons with similar chemical properties and containing carbon atoms joined by a single pair of shared electrons (a single bond). This series is called the *methane series* or *paraffin series*. The word *paraffin* is derived from the Latin *parvum affinis*, which means "little affinity" and is a fairly accurate commentary on the chemical reactivity of these compounds. Compounds of this type react by substitution because they contain only single bonds; a hydrogen atom must be replaced or substituted when a reaction takes place. Thus the reaction is said to be one of substitution, and the compounds are *saturated*.

The following formulas represent the structures of some of the lower molecular weight paraffin hydrocarbons. The student should recognize by this time the difficulty of representing a three-dimensional body in

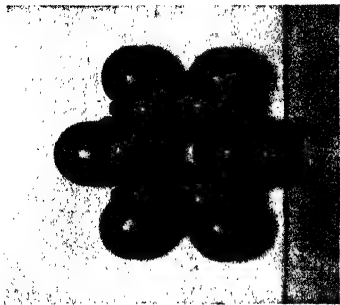
print. The spatial relations of the atoms in molecules are better but less conveniently portrayed by the scale models pictured in Fig. 165.



A number of facts pertaining to paraffin hydrocarbons may be deduced from these formulas and names. It should be noted, for example, that all the names end in *-ane*; this is typical of the names of paraffin hydrocarbons. Above butane the prefix of the name indicates the number of carbon atoms (C_5H_{12} *pentane*, C_6H_{14} *hexane*, C_7H_{16} *heptane*, etc.). When the carbon atoms are in a straight chain, unbranched, they are called *normal* hydrocarbons (for example *n*-pentane). If the



n-Heptane



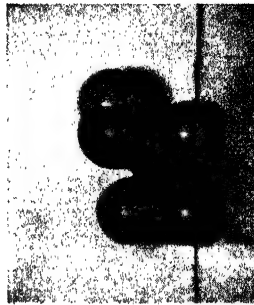
Benzene



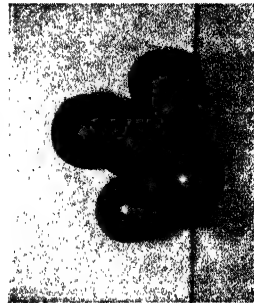
2,2,4-Trimethylpentane
"Iso-octane"



Ethyl chloride



Ethyl alcohol
"Alcohol"

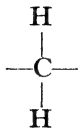


Acetic acid

Figure 165. Models of some common organic compounds.

carbon chain is branched, they are frequently called *iso* hydrocarbons (*e.g.*, *isopentane*).

From the molecular formulas of the compounds it is evident that each member of the paraffin series differs from the preceding member by 1 carbon atom and 2 hydrogen atoms.



When compounds constitute a series of this type, they are said to be *homologues* and the series a *homologous series*. The general formula of the paraffin series is $\text{C}_n\text{H}_{2n+2}$.

The knowledge that members of a homologous series have, in general, the same chemical properties goes a long way in easing the burden of learning organic chemistry.

The physical properties of the paraffin hydrocarbons vary in a regular way with their molecular weight. The four lightest members are gases, the next ten are liquids, and those of higher molecular weight are solids. There are generally some variations caused by differences in structure; but, in general, the boiling point of a hydrocarbon is determined by its molecular weight (carbon content)—the higher the molecular weight, the higher the boiling point.

There are no isomeric forms of methane, ethane, or propane, but starting with butane the number of possible isomers increases strikingly with increase in carbon content. The formulas of the isomers of butane and pentane have already been given. There are 5 isomers of hexane, 9 isomers of heptane, 75 isomers of decane, 366,319 isomers of $\text{C}_{20}\text{H}_{42}$, and 4,111,846,763 isomers of $\text{C}_{30}\text{H}_{62}$. Most of these, of course, have not been synthesized in the laboratory or found in nature, although all those of low molecular weight are known. These data should clearly indicate that isomerism plays an important role in accounting for the large number of organic compounds known.

The only important source of paraffin hydrocarbons is petroleum. The importance of petroleum as a source of these hydrocarbons will be discussed in the next chapter, along with their use as fuels. Paraffin hydrocarbons are also used as raw materials for the production of

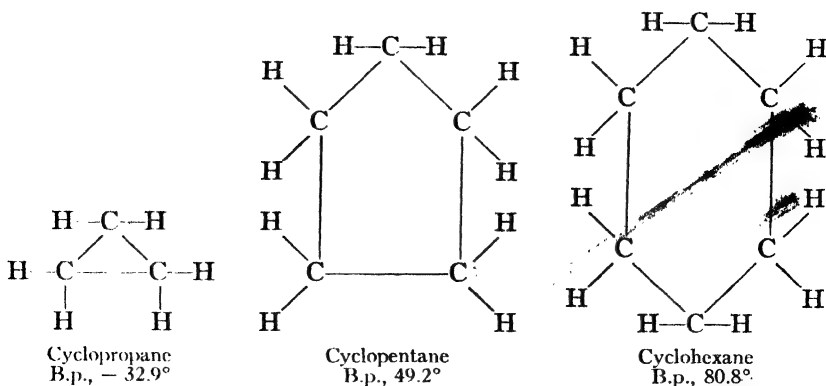
many other compounds. These reactions will be noted in the following chapters where the particular compound synthesized is discussed.

Cyclic Hydrocarbons (Naphthenes). The cyclic hydrocarbons (*naphthenes*) are similar to the paraffin hydrocarbons except that instead of being open-chain (either straight or branched) compounds their carbon



Figure 166. Storage containers for normally gaseous hydrocarbons. (Courtesy of the Shell Oil Company, Inc.)

atoms are arranged in closed-chain or ring structures. The following three compounds are important cyclic hydrocarbons:

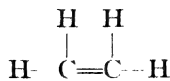


These compounds are relatively stable and are considered saturated hydrocarbons because they react by substitution even though the type formula for these hydrocarbons is C_nH_{2n} , that is, the same as that of the olefins (*vide infra*).

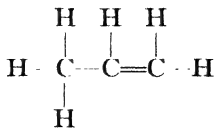
The principal source of naphthenes is petroleum, although some are synthesized from other compounds. They do not have many important uses other than as components of gasoline, kerosene, etc., and for the synthesis of a few compounds. *Cyclopropane* is used as an anesthetic.

Olefins. The hydrocarbons studied thus far have all been characterized by having the carbon atoms joined by only two electron bonds—single bonds. Another possible series of hydrocarbons is that wherein two or more of the carbon atoms share two pairs of electrons to form a *double bond* ($\cdot\dot{C}=\dot{C}\cdot$). Compounds of this type are characterized by their ability to react by addition and thus are said to be *unsaturated*. This ability to add reagents is characteristic of compounds with either double or triple bonds, while the paraffin hydrocarbons can react only by substitution. This difference in type of reaction is frequently used to determine whether or not a certain compound is saturated or unsaturated.

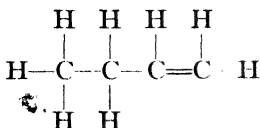
There are many different hydrocarbons containing double bonds, but only the following are of importance here:



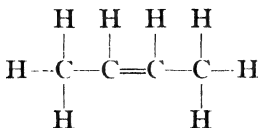
Ethylene
(Ethene)
B.p., -103.9°



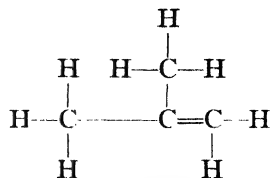
Propylene
(Propene)
B.p., -47.6°



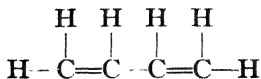
1-Butene
B.p., -6.3°



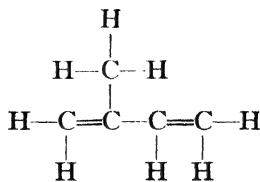
2-Butene
B.p., 1°



Isobutylene
B.p., -6.9°



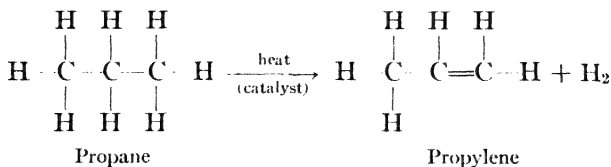
Butadiene
B.p., -4.5°



Isoprene
B.p., 34.1°

These compounds are *olefins* and are usually called *ethylenic hydrocarbons*, not only because ethylene is the first member of the series, but also because it is the most important. Frequently the first member of a homologous series of compounds gives its name to the whole series. The type formula of olefins is C_nH_{2n} when there is only one double bond in each molecule.

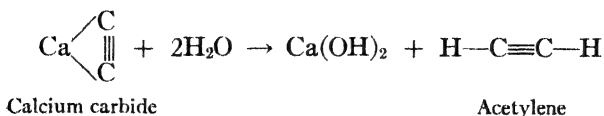
The lower molecular weight olefins are not directly available from nature but may be produced from the corresponding paraffin hydrocarbon by removing two atoms of hydrogen.



Other atoms or groups of atoms also may be removed to form olefins. These reactions are used for laboratory preparations of olefins and will be noted in subsequent chapters. Olefins are produced industrially as by-products during the manufacture of gasoline from petroleum (Chapter 25); consequently the lower molecular weight olefins are available in large quantities at a low cost.

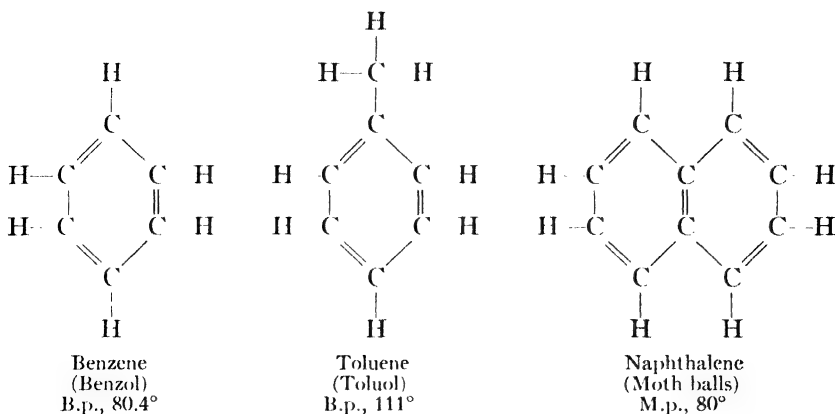
With the exception of ethylene, olefins have few important uses other than in the production of compounds of more value. The olefins are frequently called the link between the relatively unreactive, naturally occurring saturated hydrocarbons and many of the multitude of chemical compounds to which we shall refer in the remaining chapters. Ethylene is used, with oxygen, as an anesthetic; and because it also possesses hormone-like properties it is used to ripen fruit, especially citrus fruit. Isoprene is the building unit of natural rubber, and butadiene is used for the production of synthetic rubber.

Acetylenes. Acetylene is the first and by far the most important member of a homologous series of hydrocarbons containing a triple bond and having the type formula C_nH_{2n-2} . It is produced by the action of water on calcium carbide (from limestone and coal).



Acetylene is used as a fuel in the oxyacetylene torch and for the production of a number of useful chemicals.

Aromatic Hydrocarbons. This rather small but very important class of hydrocarbons has as its type formula C_nH_{2n-6} , with the lowest member, *benzene* (benzol), having the formula C_6H_6 . In spite of this obvious unsaturation, benzene and its homologues react predominantly by substitution instead of by the addition reactions that are typical of unsaturated compounds. This anomalous chemical behavior has resulted in much research on the structure of these compounds. For most purposes the structure given for each of the following three important aromatic hydrocarbons is adequate to represent the molecules:



The alternate single- and double-bond arrangement in a six-carbon hydrocarbon gives the double bond a unique resistance to addition reactions.

Both benzene and toluene occur in petroleum to some extent and are synthesized from certain other constituents of petroleum. The principal source of aromatic hydrocarbons, however, is *coal tar* (Chapter 28), a mixture of a number of chemicals obtained when coal is heated in the absence of air to produce coke. One ton of coal will yield approximately 150 pounds of coal tar. This would not be a very fruitful source of various compounds if it were not for the fact that 100,000,000 tons of coal is converted to coke each year.

The aromatic hydrocarbons are not used as fuels because they are much more valuable as raw material for the production of many com-

pounds. This is especially true of benzene, from which are made most of our dyes and many of our medicinals, plastics, perfumes, and explosives. Benzene, toluene, and some closely related compounds are also used as solvents and diluents by the paint and varnish industry (Chapter 32) and to some extent as additives to gasoline (Chapter 25).

EXERCISES

1. *New terms:* organic chemistry, single bond, double bond, triple bond, hydrocarbon, paraffin hydrocarbon, homologue, homologous series, normal hydrocarbon, iso hydrocarbon, cyclic hydrocarbon, naphthene, olefin, unsaturated hydrocarbon, ethylenic hydrocarbon, acetylenic hydrocarbon, aromatic hydrocarbon, coal tar.
2. Who may be considered the father of organic chemistry?
3. Name a natural source of urea.
4. Draw diagrams representing the structure (complete with electrons, protons, and neutrons) of an atom of each of the following elements: carbon, hydrogen, sulfur, nitrogen, chlorine, and bromine.
5. State the "rule of two."
6. Indicate four ways in which organic compounds differ from inorganic compounds.
7. List five objects made of or containing organic compounds that are within reach as you read this sentence.
8. Account for the lack of reactivity of paraffin hydrocarbons.
9. Why are olefins more reactive than paraffins?
10. Draw the structural formulas of three members of a homologous series.
11. Draw the structure of each of the isomers of hexane.
12. Give an important natural source of each of the following types of hydrocarbons: (a) paraffin; (b) aromatic; (c) naphthene.
13. Write an equation indicating a method of producing (a) an olefin; (b) acetylene.
14. Give two important uses of each of the following compounds: (a) benzene; (b) acetylene; (c) ethylene.
15. Approximately how many tons of coal tar are produced each year?

COLLATERAL READING

BREWSTER: "Organic Chemistry," Prentice-Hall, Inc., New York, 1948, Chapters 1-4, 23, and 24.

CONANT and BLATT: "The Chemistry of Organic Compounds," The Macmillan Company, New York, 1947, Chapters 3, 4, and 21.

FIESER and FIESER: "Organic Chemistry," D. C. Heath and Company, Boston, 1944, Chapters 1-4, 12, and 19.

WILLIAMS and HATCH: "Introduction to Organic Chemistry," D. Van Nostrand Company, Inc., New York, 1948, Chapters 1, 2, 4, and 21.

Petroleum. Fuels

Thus far in organic chemistry we have studied the simplest and in some respects the most important organic compounds - the hydrocarbons. Before proceeding with the study of compounds related to the hydrocarbons, consideration should be given to the occurrence of hydrocarbons in nature and their uses.

Petroleum. These compounds have as their principal source a dark greenish-brown liquid called petroleum (from the Latin *petra*, a rock; *oleum*, oil), literally rock oil, but more commonly *crude oil*. At the present time most of the 200 million gallons of petroleum produced in the United States each day is used for heating, lighting, and power. Less than 1 per cent of this petroleum is used for the synthesis of other chemicals, but this amount makes possible the production of about 10 million pounds of organic chemicals per day. The importance of petroleum in our time can hardly be overemphasized.

It is obvious that material produced in this quantity must be important, not only as a source of hydrocarbons, but also for its role in the nation's economy and way of life. It also affects all of us in a very personal way as the provider of the fuel for our automobiles, heat for our houses, and plastics for the boudoir and elsewhere, to mention only a few uses. The tremendous expansion of the petroleum industry in the last ninety years has been concomitant with correspondingly great technological advances in other fields. Petroleum has not been the basis of all of the technological advance of modern civilization, but it has made a significant contribution. It should also be noted that modern warfare could not be waged without petroleum.

Historical. Petroleum has been known for as long a time as gold and silver and for the same basic reasons: it appears on the surface of the earth, and it is stable. Many petroleum-bearing vessels have been found dating from the time of Abraham, and more than 7000 years

ago the Egyptians used petroleum in their famous embalming process. The bricks in the wall around Babylon were held together with an oil composition, and the peripatetic Phoenicians 5000 years ago calked their boats with an oil product. As early as 200 B.C. the Chinese drilled for oil to use as a fuel, even as we do today. Constantinople (Istanbul) was defended from the Crusaders by flame throwers. Marco Polo in the thirteenth century reported a pool of oil in Armenia which was good for "Burning and for the cure of distemper in man and cattle"—still two important uses of petroleum. Three centuries ago there was an extensive oil industry at Baku on the Caspian Sea.

Although petroleum had been known in this country since 1627, the first oil well was not drilled until 1859. At Titusville, Pa., on Aug. 27, 1859, oil was struck at a depth of about 70 feet, and the well produced 630 gallons of oil per day (Fig. 168). The modern petroleum industry had been born; and within a year it was predicted that if they continued to take oil out of the ground at that rate our petroleum supplies would be exhausted in five years. These predictions are still being made, and some time may come true.

The early refinery practice was to produce kerosene from petroleum to be used as an illuminant and for heating. The industry was relatively stable until the tungsten-filament electric-light bulb made kerosene lamps obsolete. Fortunately for the petroleum industry the horseless carriage, which required gasoline for its internal-combustion

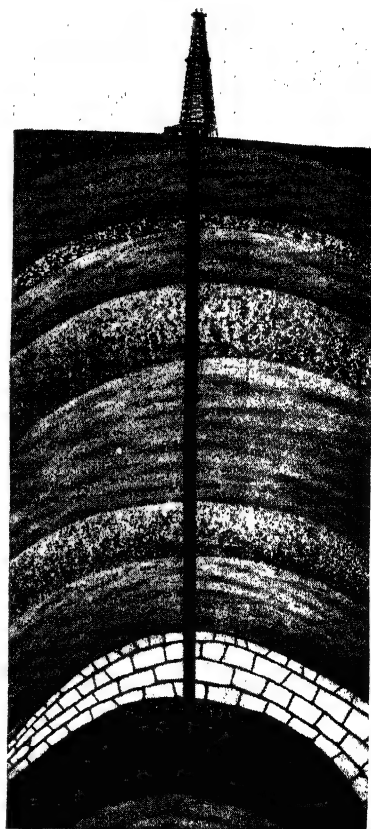


Figure 167. Drawing of an oil well, showing the type of formation in which oil is found. (*Courtesy of the Oil Industry Information Committee.*)

engine, was developed during this period. Refinery practice was changed to meet the new demand, and the petroleum industry expanded instead of becoming the victim of progress in the illuminating industry. The production of gasoline is still the major business of the petroleum



Figure 168. View of Drake well located at Titusville, Pa., completed in 1859. Colonel Drake is wearing the tall hat. (*Courtesy of the Sun Oil Company.*)

industry, but many other petroleum products are also produced, as well as many organic chemicals by synthesis.

The production of petroleum has spread from Pennsylvania over the entire United States. By contrast with the original 70-foot well, oil wells are now commonly drilled to 10,000 feet, with some wells as deep as 15,000 feet.

Our dependence on petroleum was amply shown during World War II. It is perhaps fortunate that petroleum has the world-wide distribution indicated in Fig. 169.

The Nature of Petroleum. Petroleum is a very complex mixture of hydrocarbons containing mainly paraffin hydrocarbons and some naph-

thenes and aromatic hydrocarbons with molecular weights from the lightest to over 600. The nature of these hydrocarbons varies within rather wide limits depending upon the origin of the petroleum. No two oil fields produce exactly the same crude oil. In addition to the



Figure 169. World distribution of petroleum. Each x represents an area producing an appreciable quantity of petroleum.



Figure 170. General view of a typical petroleum refinery. (Courtesy of the Shell Oil Company, Inc.)

hydrocarbons there are also present compounds containing oxygen, sulfur, and nitrogen. The amount of these non-hydrocarbons also varies widely depending upon their source; they usually do not constitute more than 10 per cent of the compounds present.

Petroleum as it comes from the ground is of little value. It must be separated into fractions or groups of compounds possessing approximately the same physical properties. The process of making crude oil into articles of commerce is called *refining* (Fig. 170). The earliest

method of refining was simple distillation, and this operation is still the initial refining step.

Distillation. The process of distillation is very important, not only in the refining of petroleum, but also in the whole organic chemical industry, where it is used for the separation and purification of com-

pounds. Distillation consists in the vaporization of a substance, either a liquid or a solid, and the condensation of the vapor in a vessel other than the one used for the vaporization. A single, organic substance is readily distilled with an ordinary distillation apparatus not greatly different from those used hundreds of years ago in Europe (Fig. 171).

In both laboratory and technical operations there often arises the problem of separating by distillation a mixture of two or more liquids, all of which are present in appreciable amounts. The separation of such a mixture into various fractions, some of which are rich in a particular component, often may be achieved by what is termed *fractional distillation*. Fractional distillation consists essentially in the systematic redistillation of distillates (fractions of increasing purity). Fractionations can be carried out using simple apparatus, but in cases where the components do not have widely separated boiling points it is a very tedious process. A device known as a fractionating column (Fig. 172) very greatly simplifies the procedure. A fractionating column is essentially an apparatus for performing a large number of successive distillations without the necessity of actually collecting and redistilling the various fractions.

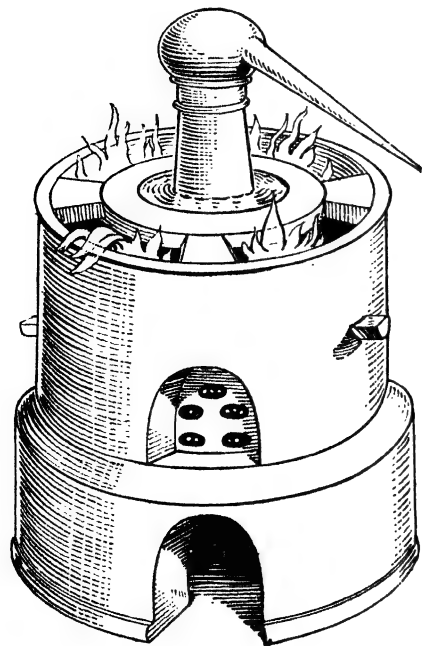


Figure 171. Distillation apparatus of the sixteenth century.

Distillation of Crude Oil. Because petroleum is a mixture, it is theoretically possible to separate it into its components by the physical

means of distillation. There are so many different isomeric compounds in petroleum, however, that it is impossible to separate each individual compound. In fact, many of these different compounds have the same boiling point. Fortunately, a complete separation is not necessary for the use of petroleum as a fuel, because the use of various fractions for



Figure 172. Modern fractionating columns or stills used in the separation of petroleum fractions. (Courtesy of the Shell Oil Company, Inc.)

this purpose is based primarily on volatility or boiling range. A mixture of hydrocarbons will usually serve as well as an individual compound as long as the mixture has comparable physical properties.

Table 10 gives an indication of the broad fractions into which petroleum is separated by distillation. These fractions are rather flexible as to their upper and lower boiling limits.

The *liquefied gases* obtained from petroleum consist of propane and butane with lesser amounts of ethane and pentane. They are used in the synthesis of aviation gasoline, synthetic rubber, and numerous

TABLE 10. Petroleum Fractions

Name of fraction	Carbon content	Boiling range, degrees centigrade	Uses
Liquefied gases	C ₁ to C ₄	Below 0	Fuels, syntheses
Petroleum ether . .	C ₅ to C ₆	20 to 60	Solvents, syntheses
Light naphtha	C ₆ to C ₇	40 to 90	Solvents
Gasoline	C ₆ to C ₁₂	40 to 220	Fuel (engine)
Kerosene	C ₁₁ to C ₁₈	175 to 325	Fuel (diesel and jet engine), cracking
Gas oil	C ₁₆ —	Above 275	Fuel, cracking
Lubricating oils	C ₁₇ —	Above 300	Lubricants
Residuum	Petrolatum (vaseline), paraffin wax, road oils, asphalt, coke, etc.

compounds that will be mentioned later. The liquefied gases are also sold extensively as household fuels and are designated as *bottled gas*.

Petroleum ether and *light naphtha* are liquids too high-boiling to be used as gaseous fuels and too low-boiling to be used as liquid fuels. The pentanes, hexanes, and heptanes contained in these fractions are frequently separated into individual compounds by distillation and used for synthesis of more desirable compounds. The mixtures are used as inexpensive solvents and diluents in the paint and varnish industry (Chapter 32).

Gasoline obtained by simple distillation from crude oil is called *straight-run gasoline* and consists of a large percentage of normal paraffin hydrocarbons with a lesser amount of naphthenes and aromatic hydrocarbons. The relative amounts of the different hydrocarbon types vary widely depending upon the particular oil field from which the crude oil comes. This fraction is used as a fuel for internal-combustion engines having a spark ignition (automobile and airplane engines) and for little else. Because gasoline is the most important fraction of crude oil, it will be discussed more fully later in this chapter.

Kerosene is used as an illuminant in oil lamps and as a fuel for diesel engines and for jet and turbo-jet engines; its main advantage is its low cost. Because of the low volatility of kerosene it is not suitable for automobile engines although it can be used at an appreciable sacrifice of efficiency. *Gas oil* is used as an industrial and domestic fuel for heating purposes and for the preparation of oil gas. It is also used for the synthesis of gasoline by several processes that will be discussed later.

Lubricating oils obtained from petroleum are many in number and vary widely in character. There is an oil for every conceivable use and at prices from a few cents a gallon (used for oiling wagon wheels) to a hundred dollars or more an ounce (such as that used for precision instruments, *e.g.*, watches). Modern civilization is dependent upon many things, not the least of which is its lubricating oils. A noted general once observed that an army travels on its stomach—a modern army also moves on its lubricants.

Early refining practice produced an oil having a characteristic yellow-green fluorescence. Most lubricating oils could now be furnished to the public in the form of nearly water-white liquids, but the oils are dyed the color that the consumer has learned to associate with oiliness. Over six million gallons of lubricating oils is produced in the United States each year.

The *residuum* that cannot be distilled is usually classified as either asphaltic or paraffinic in nature, which leads to a classification of crude oil as either asphalt base, paraffin base, or mixed base crude, depending upon the nature of its residuum. Pennsylvania oils are paraffin base, while most of the other United States oils are either mixed base or asphalt base; California oils are mainly asphaltic. These classifications are of importance in determining the method of refining to be used.

A semi-solid product of the residuum from paraffin-base oils is called petrolatum and is sold as a medicine under various names, of which *vaseline* is probably the best known. *Paraffin* is also obtained from this type of oil. Asphaltic oils yield a thick black pitch called *asphalt* that is used for roofing and paving.

Non-hydrocarbon Compounds. The oxygen, sulfur, and nitrogen compounds are, in general, of complex nature as they occur in petroleum, but they tend to break down into smaller molecules during the distillation of the crude oil. The sulfur compounds are especially undesirable in gasoline because they decrease the effectiveness of tetraethyl lead, a compound added to improve the quality of the gasoline. They also have an unpleasant odor and are often corrosive. The sulfur compounds are either removed by extraction or oxidized to less odorous compounds (Fig. 173). The extraction process consists in treating the gasoline with a water solution of a base with which the acidic sulfur compounds react; this process also removes the oxygen compounds

because they are acidic in nature. Several other methods of refining gasoline are used.

The sulfur compounds have little economic value, but the oxygen compounds are quite valuable and will be mentioned in later chapters. The nitrogen compounds are usually not removed.

Gasoline. All of the 90 million gallons of gasoline produced daily in

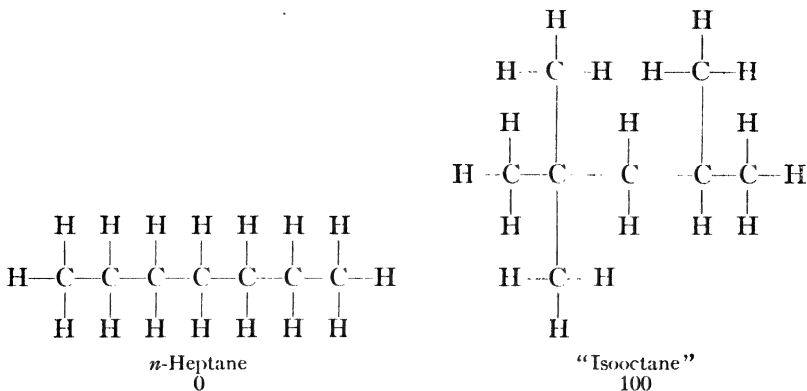


Figure 173. Catalytic desulfurization unit. (Courtesy of the Phillips Petroleum Company.)

the United States are not from the same type of crude oil; consequently their composition and quality will vary widely. In fact, much of this gasoline is not even the product of direct distillation of crude oil; rather it is manufactured by various methods that produce different qualities of gasoline. Because of these differences in quality it early became necessary to have some basis or measure of quality to ensure uniformity in the final product.

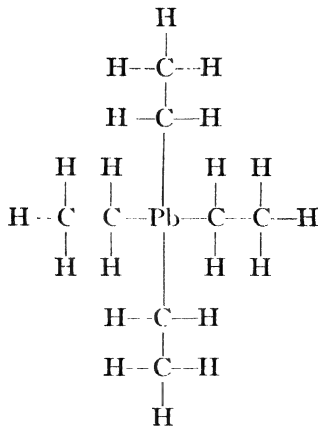
It has long been recognized that the structure of a paraffin hydrocarbon determines its efficiency in an automobile engine. The normal (straight-chain) hydrocarbons are very poor fuels and cause the motor to "knock," while highly branched chain paraffins are very satisfac-

tory. An arbitrary scale has been established with *n*-heptane given an *octane number* of 0 and "isooctane" an octane number of 100 (see Fig. 165, Chapter 24).



A gasoline is said to have an octane number of 80 when it is as good as a mixture of 20 per cent *n*-heptane and 80 per cent isooctane. The higher the octane number, the better the gasoline; and it is possible to have compounds and gasolines that have an octane number over 100 or below 0. It is not economically sound, however, to use a grade of gasoline better than the lowest that can be used without knocking.

During the early part of the present century the petroleum industry was able to supply the nation's gasoline needs by straight-run gasoline. A typical crude oil contains about 20 per cent gasoline. Around 1920 the demand for gasoline increased to a point where crude oil could not be distilled in sufficient quantity to meet it; the problem of what to do with the higher fractions also became acute. A solution to both problems was found in the process known as *cracking*. The higher molecular weight hydrocarbons were subjected to heat and pressure, which caused them to break into fragments, some of which boiled in the gasoline boiling range. There were also formed molecules of even lower boiling points, which at the time were used as a gaseous fuel. This *cracked gasoline* was blended with straight-run gasoline and resulted in sufficient gasoline to take care of the current needs. The gasoline of this period was not of good quality but was adequate for the requirements of the time. It was discovered in 1922 that 1 to 3 ml. of *tetraethyl lead* added per gallon of gasoline materially improved its quality, which

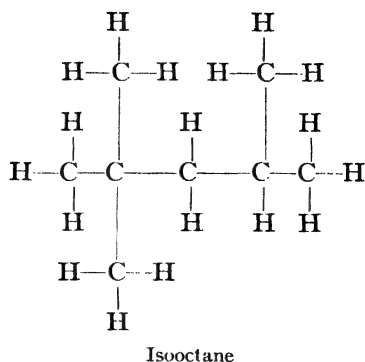
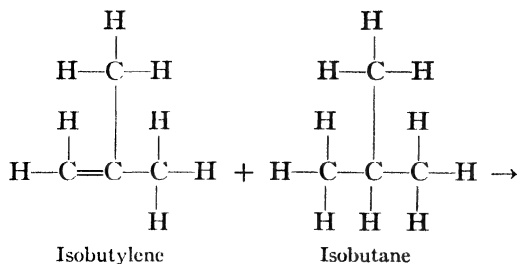


in turn permitted the automotive engineer to design more efficient engines. This method of improving gasoline is still in use, and the resulting product is *ethyl gasoline*. Tetraethyl lead is poisonous, and leaded gasoline should never be permitted to come in contact with the skin.

No material changes were made in gasoline manufacture until it became apparent just before World War II that a much better gasoline must be produced for use in airplane engines. This gasoline was obtained by taking two compounds of lower molecular weight than those in gasoline and causing them to join together in the presence of cold concentrated sulfuric acid, as shown in the equation on page 393. During World War II this method was improved by using HF in place of H_2SO_4 as the catalyst, but in either case the product is called *alkylate* or *aviation gasoline*. The term aviation gasoline is a loose one applied to any high-octane gasoline suitable for airplane engines.

During World War II the old process of heat cracking was improved upon by the use of catalysts. It is now possible not only to make little molecules out of big molecules, and vice versa, but also to make branched-chain molecules out of straight- (normal) chain ones all more or less at the same time (Fig. 174). Automobile gasoline is a blend of gasolines made by all of the various methods, and the ratio varies with the season. In the winter a more volatile gasoline is desirable for easier starting; in the summer a gasoline of this type would evaporate too easily.

At the present time it is possible to convert 85 per cent of a gallon of crude oil into gasoline if all the available techniques are used.



Natural Gas. The other source of paraffin hydrocarbons is *natural gas*, a rather general term for any gas that is obtained from the ground. We shall restrict the term, however, to those gases containing predominantly methane with small amounts of ethane, propane, and higher hydrocarbons. A typical natural gas might have the following composition: methane, 85 per cent; ethane, 8 per cent; propane, 4 per cent; butane, 1.5 per cent; higher hydrocarbons, 1.5 per cent. The relative amounts will vary widely from one gas field to another, but methane is always the main constituent.

Natural gas is widely distributed throughout the United States, 37 states producing over 4,000,000,000,000 cubic feet each year with Texas, Louisiana, and California the principal producing states. Most of this natural gas is used as a fuel or for the manufacture of carbon black, and the higher boiling constituents are removed and sold as natural gasoline. This type of gasoline is too low-boiling to be used by itself, but it may be blended with other types of gasoline. About 11 per cent of our gasoline is *natural-gas (casing-head) gasoline*.

A recent development in the utilization of natural gas for synthesis

is the *Fischer-Tropsch* process, which originated in Germany. In this process, gasoline, diesel oil, and many organic chemicals are produced by first changing the natural gas to carbon monoxide and hydrogen, then passing this mixture over a catalyst. One plant alone has an annual capacity of over 152 million pounds of chemicals. Natural gas

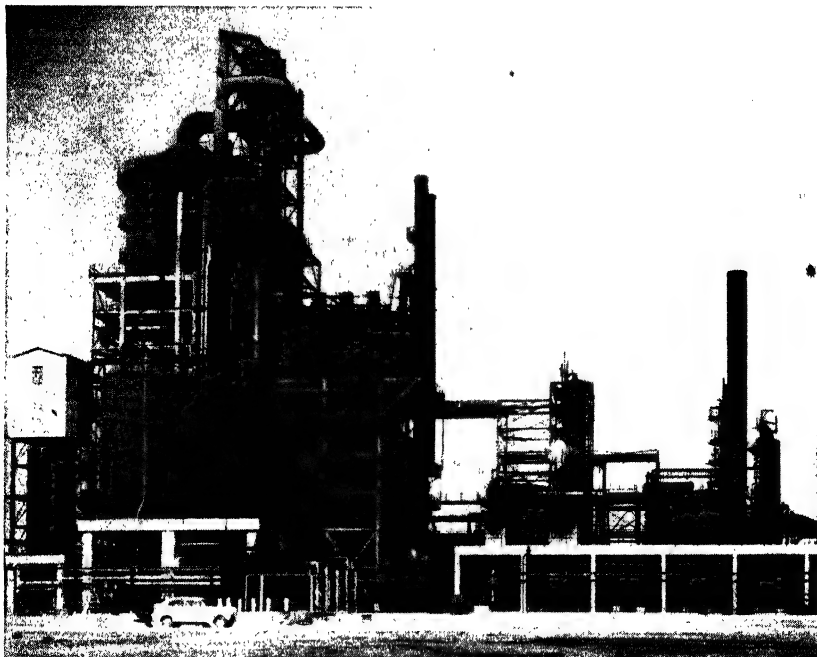


Figure 174. Fluid catalytic cracking unit used in the production of 100-octane aviation gasoline. Note the size of the unit compared to the automobile in the foreground. (Courtesy of the Pan American Refining Corporation.)

is also oxidized in the presence of a catalyst to produce many chemicals, about 10 per cent of the natural gas produced being utilized in the production of other chemicals by this and other methods.

Petrochemicals. Petrochemicals are those which are obtained either directly or indirectly from petroleum or natural gas. The production of chemicals is the result of the recent realization by both chemical and petroleum companies that in the hydrocarbons there are vast possibilities for synthesis of more valuable compounds.

The first chemicals were made from petroleum in 1925. Table 11

gives an indication of the rapid growth of this industry in recent years.

TABLE 11. Production of Petrochemicals*

<i>Year</i>	<i>Petrochemicals, pounds</i>
1925	150,000
1942	500,000,000
1943	1,564,915,000
1944	2,804,625,000
1945	3,300,000,000
1946	3,800,000,000

* From *Chemical and Engineering News*, **25**, 3634 (1947)

The petrochemical industry is still in its infancy. The number of oil companies classified as chemical producers has increased, however, from 1 in 1935 to over 50 in 1946; and at present over 30 per cent of all organic chemicals are derived from petroleum or natural gases. Less than 5 per cent of the annual production of petroleum would be sufficient to manufacture all the organic chemicals needed in the United States.

The Southwest is the fastest growing chemical area in the United States, for it produces over 60 per cent of the country's crude oil and 71 per cent of its natural gas. In addition to these it also contains 20 per cent of the country's salt and practically all of its sulfur, both of which are basic raw materials for inorganic chemicals. The future of chemistry in this area is amply shown by an investment of over \$340,000,000 that has been made in installing chemical plants in the Texas Gulf area during 1947 and 1948.

Petroleum Reserves. With such a large amount of crude oil and natural gas being taken out of the ground each year, the question naturally arises as to how long it will last. The proven reserves of liquid hydrocarbons in the United States are about 1,050,000,000,000 gallons, and the proven natural gas reserves are about 160,000,000,000,000 cubic feet. Assuming no change in the amount of crude oil used each year and no new reserves discovered, this amount of liquid hydrocarbons will last 15 years, and the natural gas will last 44 years.

Many factors will combine to extend this period, such as the hydrogenation of coal and the Fischer-Tropsch process, which produces gasoline from natural gas at a cost of about 6¢ a gallon. And, of course, there will be new oil fields discovered, as there always have been. This

cannot go on for an indefinite period of time, although some authorities claim that petroleum is being formed at the present time faster than it is being used.

There are also enormous deposits of oil shale from which petroleum may be obtained if necessary. It is estimated that this source alone could supply our needs for 400 years. Different types of fuels may also be used, such as ethyl alcohol made from farm products, or Gasogene, a gaseous fuel from charcoal.

Fuels. The term *fuel* is applied to materials used to produce heat (energy) by a chemical reaction with air. Man is unique among animals in his ability to utilize fuel to create heat and power. Because of this ability he has improved vastly his means of procuring food, raised his standard of living, and made it possible to live on almost the entire area of the earth. It has also made possible his waging ever increasingly destructive wars. The main materials that he has adapted for his use as fuels are coal, wood, peat, oil, and natural gas, all of which are made up of hydrogen compounds of carbon and their derivatives.

The emphasis placed upon petroleum as a fuel might lead one to believe that it is by far the most important source of energy. This may be true in the future, but at the present time oil and gas account for only 48 per cent of the United States energy production, while coal accounts for an equal amount and water power furnishes the remaining 4 per cent. From the standpoint of world energy production, coal is, however, by far the most important and probably will remain so for some time to come. It should be noted that each day the sun furnishes the United States with 1000 times the combined energy of all the afore-mentioned sources. •

Solid Fuels. Solid fuels may be classified as being either "natural" or "manufactured." The natural fuels are coal, wood, peat, and other vegetable matter, while the principal manufactured fuels are coke and charcoal, which are essentially carbon and have been noted in Chapter 26.

Coal. Coal is by far the most important soil fuel. It is formed by the action of decay, heat, and pressure upon vegetable and woody material deposited a great many years ago. Coal varies widely in composition and properties, as would be suggested by its variegated antecedents. The most important types are peat, lignite, bituminous (soft) coal,

and anthracite, or hard coal. Table 12 gives an indication of the composition of a typical example of each kind.

TABLE 12. Composition of Solid Fuels, Percentage

	Carbon	Hydrogen	Oxygen	Ash
Wood.....	48.5	6.0	43.5	1.5
Peat.....	58.0	6.3	30.8	4.0
Lignite.....	68.0	5.1	19.5	6.3
Soft coal.....	82.0	5.0	6.0	7.0
Hard coal.....	90.0	2.5	2.5	4.0

Vast *peat* bogs occur in the temperate humid climates of the world, formed by the accumulation and partial decomposition of vegetable matter under marshy conditions. The utilization of peat is extensive only where there is a deficiency of coal, and its chief use is as a domestic fuel.

About 50 per cent of the world's coal reserves consists of *lignite*, and this remains relatively unexploited. It is decidedly inferior to the widely used *bituminous*, or soft, coal, which burns with a smoky yellow flame because of its high content of volatile compounds. The numerous varieties of bituminous coals are notable also for their resistance to weathering. The much less abundant *anthracite* coal contains but little volatile matter, has a high calorific value, and is the kind most valuable for industrial use.

The world coal reserves are estimated to be sufficient for the next 1000 years.

Wood. Wood is undoubtedly the first fuel used by man, and it is still used in large quantities, although industries have changed over to coal, oil, and natural gas. The main drawbacks to using wood are its lower calorific value and the high cost of transporting it large distances by rail. The principal use of wood is as a domestic fuel, the soft resinous varieties such as fir, spruce, and pine being the most desirable.

The flame of burning wood may be colored by impregnating the wood with nitrates of strontium (red flame), copper (green flame), calcium (brick-red flame), potassium (pale violet flame), etc.

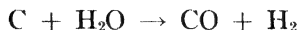
The combustion of these solid fuels is a very complex process that takes place in several steps involving gases, water vapor, and solid carbon. The fuel must first be heated to the point of decomposition, where various gases are evolved. These gases vary in composition but

are chiefly hydrocarbons, hydrogen, carbon monoxide, water, tarry material, and finely divided carbon. It is these gases and the carbon which burn. The light is usually provided by incandescent carbon particles.

Liquid Fuels. Although the extensive use of liquid hydrocarbons for fuel is of very recent origin, the use of liquid fuels dates back to very ancient times, when vegetable and animal oils were burned for the production of light and to some extent for heat. These oils are of little importance for these purposes today because they have been largely supplanted by petroleum products. Ample comment has already been made on these fuels.

Gaseous Fuels. The gaseous fuels are natural gas, coal gas, water gas, producer gas, and blast-furnace gas. The last three types are obtained by partial combustion or by the action of steam on hot carbonaceous materials. *Natural gas* has been discussed earlier in the chapter. Coal gas is obtained by the distillation of coal. The distillation of coal and the compounds thereby obtained are discussed in Chapter 28.

Water gas is made by passing steam through coke at 1000 to 1200°C., and it is composed of carbon monoxide and hydrogen.



Because of the presence of carbon monoxide, this gas is very poisonous. A small amount of an odoriferous compound is added to gaseous fuels to serve as a warning agent.

Producer gas is formed by passing air through a five- or six-foot layer of coal that is burning at the bottom but not at the top. The carbon dioxide formed by the combustion is changed to carbon monoxide by the hot carbon near the top. Some coal gas is also produced along with the nitrogen originally in the air. The resulting gas is not high in heating value, but it is cheap. *Blast-furnace gas* is similar to producer gas in composition and comes from the top of a blast furnace, as the name implies (see Chapter 21).

EXERCISES

1. *New terms:* petroleum, crude oil, distillation, petroleum ether, straight-run gasoline, petrolatum, octane number, cracking, ethyl

gasoline, aviation gasoline, natural gasoline, Fischer-Tropsch process, petrochemicals, producer gas, refining, knock, fuel.

2. List five common household materials that come directly or indirectly from petroleum.
3. Give the date and location of the first oil well drilled in the United States.
4. What is the major product obtained from petroleum?
5. Name five important oil-producing areas in the world.
6. How many paraffin hydrocarbons could theoretically be in the C_{20} fraction of petroleum? NOTE: See Chapter 24.
7. Does petroleum consist only of a complex mixture of hydrocarbons? Explain.
8. Liquefied (bottled) gas contains hydrocarbons boiling between -10 and $+37^{\circ}\text{C}$. Name three compounds that may be present.
9. Why is it dangerous to use gasoline as a domestic dry cleaner?
10. Why is it undesirable to have sulfur compounds in gasoline?
11. Which of the following compounds would make good fuels for an automobile: neopentane, *n*-heptane, $C_{20}H_{42}$, toluene, tetraethyl lead?
12. List four different types of gasoline.
13. List in the order of their decreasing abundance the compounds usually present in natural gas.
14. What is the fastest growing chemical area in the United States?
15. The present proven oil reserves will last about 15 years; give several factors that may extend this period.
16. What are the main fuels?
17. What is the most important solid fuel?
18. Why is wood not an important industrial fuel?
19. Write the equation representing the production of water gas.
20. A gasoline with an octane number of 74 is as good as a fuel composed of what per cent "isooctane" and what per cent *n*-heptane?
21. A 15,000-foot oil well is how many miles deep?
22. How many gallons of gasoline are produced per year for each man, woman, and child in the United States? NOTE: Assume a population of 145,000,000.

COLLATERAL READING

BELL: "American Petroleum Refining," D. Van Nostrand, Inc., New York, 1945.

FUCHS: "When the Oil Wells Run Dry," Industrial Research Service, Dover, N.Y., 1946.

GRUSE and STEVENS: "Chemical Technology of Petroleum," McGraw-Hill Book Company, Inc., New York, 1942.

KALICHEVSKY: "The Amazing Petroleum Industry," Reinhold Publishing Corporation, New York, 1943.

SHNIDEMAN: "Gaseous Fuels," American Gas Association, New York, 1948.

Compounds Closely Related to the Hydrocarbons

NEARLY all of the organic chemicals that occur in nature, with the exception of the hydrocarbons, belong to the great classes of foodstuffs: fats, carbohydrates (sugars, cellulose, etc.), and proteins (meats). There are, however, many organic compounds produced by plants and animals that, although they may not contribute to the general physical well-being of mankind, at least make life more interesting. These are the compounds that add color and fragrance to the rose, flavor to the apple, and tartness to the lemon. The importance of these compounds lies in their ability not only to impart color, odor, and flavor to the better things for better living but also to make new and superior products when manufactured on a larger scale.

While nature is bountiful and even prodigal in her production of many types of organic compounds, she has not supplied us with anywhere near the required amount of the non-food chemicals. One reason is that for nature's purposes a little color, odor, or flavor goes a long way. But man has devised many other uses for these same compounds and similar ones. The organic-chemical industry has been developed within the last twenty-five years to supplement and improve upon nature in her manifold activities as a producer of chemicals. The chemical industry uses as its starting material those two great storehouses of chemicals—petroleum (for aliphatic chemicals) and coal (for aromatic chemicals). The relative importance of petroleum and coal as sources of these chemicals is indicated in Fig. 175. It is of interest to note the increased importance of petroleum relative to coal. This trend is also indicated in Fig. 176, and it has been mentioned in Chapter 25 in the section pertaining to petrochemicals.

The following chapters will show how the organic-chemical industry

has far outstripped nature as a producer of organic chemicals for industry, medicinal and pharmaceutical chemicals, agricultural chemi-

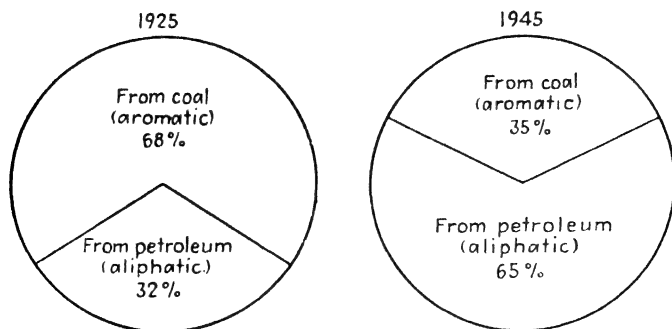


Figure 175. United States production of organic chemicals in 1925 and 1945. [From *Chemical and Engineering News*, **25**, 328 (1947).]

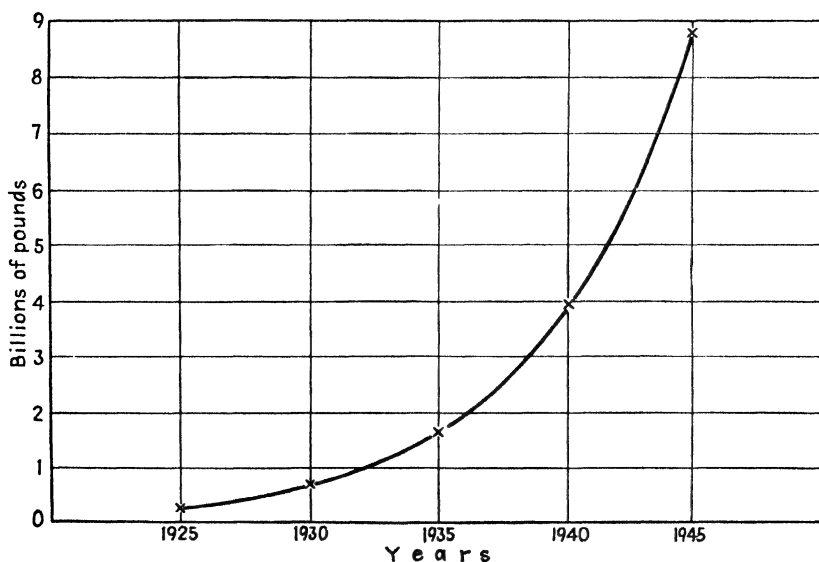


Figure 176. United States production of synthetic aliphatic chemicals. [From *Chemical and Engineering News*, **25**, 3209 (1947).]

cals, and others for special purposes. There is now produced in the United States each year 14 billion pounds of synthetic organic chemicals valued at 2 billion dollars; in 1914 there was produced only 7 million

pounds of synthetic organic chemicals valued at 3.5 million dollars. During this same period of time the number of manufacturers increased from 7 to 550. Nature is still supreme in the production of foods, feeds, and fuels.

The chemicals discussed in the present chapter are usually synthesized, for only a few of them occur in nature and then only in small

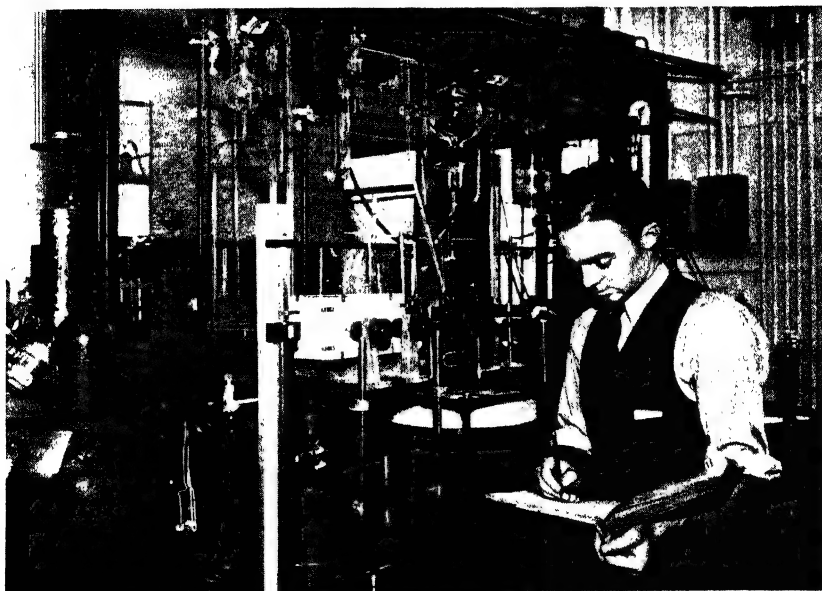


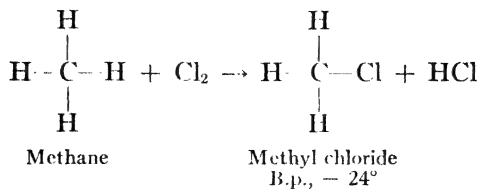
Figure 177. Research on the utilization of petroleum for the production of aliphatic compounds. (Courtesy of the Shell Development Company.)

amounts. Nearly all are derived from petroleum hydrocarbons and are related to them by having one or more hydrogen atoms replaced by some other atom or group of atoms. These compounds are usually synthesized by simple replacement reactions, although many of those which are closely related to hydrocarbons by structure are actually obtained from widely different sources or from the parent hydrocarbon by devious paths. All of these compounds are frequently referred to as *synthetic aliphatic chemicals*.

All of the production figures in this and subsequent chapters refer to United States production unless otherwise stated.

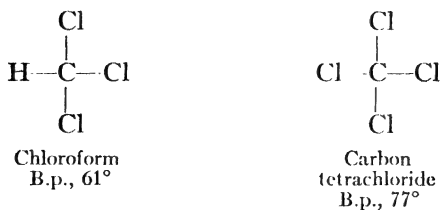
Alkyl Halides. The alkyl halides are derivatives of the paraffin hy-

drocarbons where one or more hydrogen atoms have been replaced by one or more halogen atoms. The simplest chlorine compound is that obtained by replacing a hydrogen atom of methane by a chlorine atom. This may be done by the direct reaction between methane and chlorine in sunlight at room temperature (sunlight is a powerful catalyst for many reactions in organic chemistry) or in the dark at a considerably higher temperature.



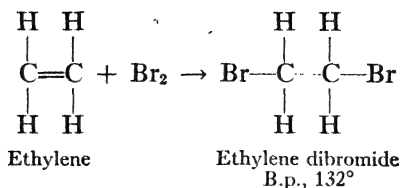
Compounds of this type are named by replacing the *-ane* ending of the hydrocarbon with *-yl* and adding the name of the halogen with its ending replaced with *-ide*. Attention is called to the similarity between the names methyl chloride (CH_3Cl) and sodium chloride (NaCl).

The remaining hydrogen atoms may be replaced one at a time, and the valuable compounds *chloroform* and *carbon tetrachloride* are produced.

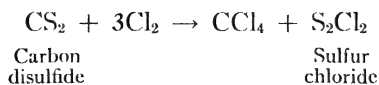


The other paraffin hydrocarbons react in a similar manner to produce a wide variety of compounds. Only the chlorides and bromides are of much industrial importance at the present time.

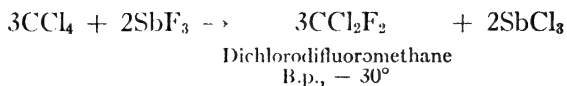
Compounds containing halogen atoms are also prepared by taking advantage of the ability of unsaturated hydrocarbons to add atoms.



Some compounds containing halogen atoms are prepared by methods that do not employ hydrocarbons directly. Nevertheless, the formal genetic relationships remain even though indirect methods are used. Carbon tetrachloride, for example, is produced to the extent of 200 million pounds per year, and most of it is prepared not from methane but rather by the action of chlorine on carbon disulfide.



Dichlorodifluoromethane (Freon-12) is prepared as indicated by the following equation:



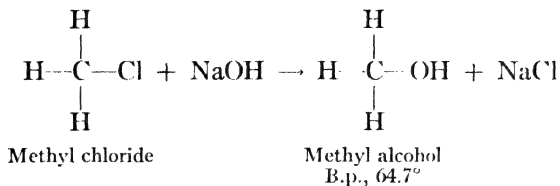
The higher boiling compounds containing chlorine atoms are frequently used as solvents for fats and oils and as dry cleaners, especially if the molecule contains more than one chlorine atom. The lower boiling compounds such as methyl chloride and dichlorodifluoromethane are used as refrigerants. Dichlorodifluoromethane was also used as the propellant in the aerosol insecticide and germicide bombs of World War II. The compounds containing both chlorine and fluorine are especially useful for these purposes because of their extreme stability, low toxicity, and low boiling point. Ethylene dibromide and dichloride are used in the ethyl fluid for ethyl gasoline (Chapter 25) because they decompose to furnish halogens, which in turn react with the lead from the tetraethyl lead to remove the metal from the engine as the volatile lead halide. They are also used as soil fumigants, as are several other similar compounds (see Chapter 31). Chlorine- and bromine-containing compounds are frequently toxic and are used as insecticides.

The alkyl halides are not used extensively for the synthesis of other compounds, for the various compounds which can be made from them can, in general, be made more cheaply by other means. An exception to this generalization is the five carbon monochlorides [*pentyl (amyl) chlorides*] that are used to make the corresponding alcohols (*vide infra*).

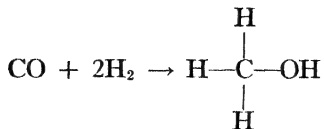
Alcohols. The alcohols (Arabic *al* and *kohl*, an impalpable powder) are compounds that may be thought of as being formed by replacing a hydrogen atom of a paraffin hydrocarbon with a hydroxyl group

(—OH). The resulting compound bears a superficial resemblance to a base (*i.e.*, CH_3OH and NaOH); but alcohols are not considered as organic bases and they are given a separate class name. There can be at least as many different alcohols as there are hydrocarbons, but only a few of these are of importance. These few, however, account for 136 million dollars worth of alcohols produced in 1947. Each alcohol will be discussed separately, because each differs in its manner of preparation and to some extent in its reactions and uses. The type formula of a simple alcohol is $\text{C}_n\text{H}_{2n+1}\text{OH}$.

Methyl alcohol (methanol, wood alcohol) is the simplest alcohol, and it is derived from methane by replacing a hydrogen atom with a hydroxyl group. This is not a reaction that can be caused to take place directly; however, by first causing methane to react with chlorine and then treating the resulting methyl chloride with a base, the desired product may be obtained.



This method of preparation is useful to illustrate the relationship of methyl alcohol and methyl chloride to methane, but it is not used industrially because methyl alcohol can be made more cheaply by the reaction between carbon monoxide and hydrogen in the presence of a catalyst.



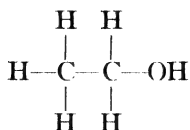
This same reaction forms the basis of the Fischer-Tropsch process for the production of many chemicals as well as hydrocarbons (Chapter 25). Different catalysts give different products. An increasing amount of methyl alcohol is being made both by the Fischer-Tropsch process and by the direct oxidation of methane under controlled conditions. About 3 per cent of the methyl alcohol produced is made by the destructive distillation of wood, and this product is given the de-

scriptive name of *wood alcohol*. Chemically, wood alcohol and methyl alcohol are identical, but wood alcohol is usually not as pure as synthetic methyl alcohol (*methanol*).

Methyl alcohol is used extensively as a solvent and as an antifreeze and in the synthesis of other compounds, many of which will be noted in this and later chapters. Between 700 and 800 million pounds of methyl alcohol is produced annually.

Methyl alcohol is poisonous and may cause blindness when used as a beverage or absorbed through the skin. It is frequently used in ethyl alcohol to make the latter unfit to drink.

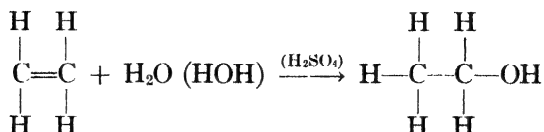
Ethyl alcohol (ethanol, grain alcohol, alcohol) is one of the most useful organic compounds and by far the most valuable alcohol.



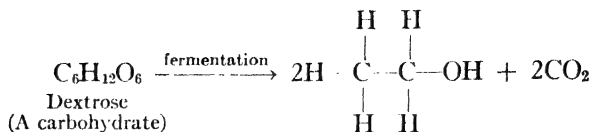
Ethyl alcohol
B.p., 78.3°

Its importance is indicated by the fact that when one speaks of "alcohol" one invariably is referring to ethyl alcohol and not to the class of compounds or to any other individual alcohol. The merit of alcohol is the result not only of its many uses but also because of its ease of preparation by the fermentation of the juices of fruits and vegetables. This ease of preparation has caused ethyl alcohol in the impure state to be known from ancient times—some believe the preparation of alcoholic beverages to be the oldest profession. Even today bushmen who do not know the relationship between father and child know how to make alcohol by fermentation. It was not, however, until 1808 that the constitution of alcohol was determined and its relationship to ethane demonstrated.

Industrial alcohol is made from petroleum by the addition of water to ethylene through the use of concentrated sulfuric acid,



and by the fermentation of carbohydrates (Chapter 29).



The Fischer-Tropsch process will also produce an appreciable quantity of industrial alcohol, but this will not be a major source until about 1952. Table 13 gives a list of the raw materials used in the production of ethyl alcohol and shows how the sources of ethyl alcohol reflect the relative costs of the various raw materials.

TABLE 13. Ethyl Alcohol, Production in Relation to Type of Raw Material

<i>Raw material</i>	<i>1941, gallons</i>	<i>1947, gallons</i>
Ethylene	69,903,000	133,306,000
Grain (carbohydrate) . .	17,532,000	39,742,000
Molasses (carbohydrate)	210,427,000	54,159,000
Unfinished spirits (carbohydrate)	49,546,000
Sulfite liquors (carbohydrate)	4,380,000
Pineapple juice (carbohydrate) . .	227,000	220,000
Whey (carbohydrate)	262,000
Potatoes (carbohydrate)	12,861,000
Miscellaneous . .	756,000	4,405,000
Total alcohol produced	298,845,000	298,881,000

Industrial alcohol is ethyl alcohol that has been distilled from a dilute water solution to a concentration of 95 per cent alcohol and 5 per cent water and that has been treated, if it were produced by fermentation, to remove any taste or odor reminiscent of its origin. Because ethyl alcohol may be used as a beverage and for this purpose is very heavily taxed, it is denatured by the addition of a poisonous or obnoxiously odored compound or compounds. These impurities usually do not interfere with the industrial uses of the alcohol; the commonly used Denatured Formula No. 1 requires 5 gallons of wood alcohol in every 100 gallons of ethyl alcohol.

A normal year's production of industrial alcohol is 200 to 300 million gallons with about 4 to 5 million gallons undenatured and tax-free for governmental, scientific, and hospital use. The general uses of denatured ethyl alcohol for a normal year and for a wartime year are given in Fig. 178.

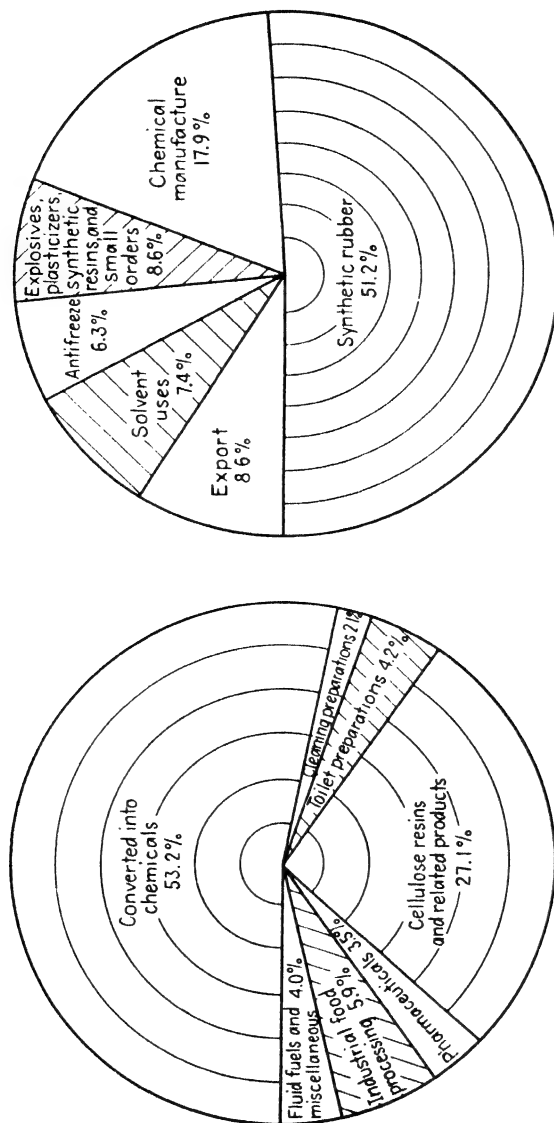
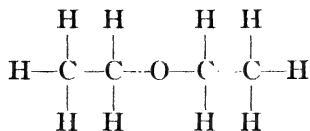


Figure 178. Uses of industrial ethyl alcohol. [From *Chemical and Engineering News*, **25**, 1794 (1947).]

An important by-product of the preparation of ethyl alcohol from ethylene is *ether* (diethyl ether), which has the following formula:

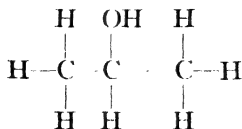


Ether
B.p., 34.6°

It may be considered as having been formed from two molecules of alcohol by the removal of the elements of water.

Ether has been used for many years as an anesthetic, but it is now being replaced by more efficient compounds of similar structure (Chapter 30). Although ether has a low boiling point and is very flammable, it is used as a solvent, especially with ethyl alcohol in the manufacture of explosives (smokeless powder).

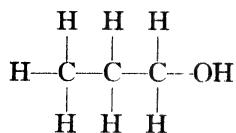
Isopropyl alcohol,



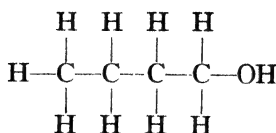
B.p., 82.3°

is made from propylene in a manner similar to that used for the preparation of ethyl alcohol from ethylene (Fig. 179). In recent years isopropyl alcohol has replaced ethyl alcohol for many of its uses, because the former has similar properties and does not have the disadvantage of government regulation for tax purposes. Isopropyl alcohol is used either alone or with methyl alcohol in the non-permanent-type anti-freeze mixtures, and as a 70 per cent solution with water it is sold as *rubbing alcohol*. It is also used as a solvent and for the production of acetone (page 416).

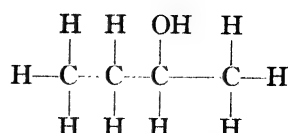
Several other alcohols are made industrially mainly for use as solvents and for the synthesis of other compounds (esters, Chapter 27) which in turn are used as solvents. The formulas of three of these alcohols and their principal method of preparation follow:



n-Propyl alcohol
B.p., 97.2°
(Oxidation of propane)



n-Butyl alcohol
B.p., 117.7°
(Fermentation)



Secondary butyl alcohol
B.p., 99.5°
(Butylene + H₂SO₄)

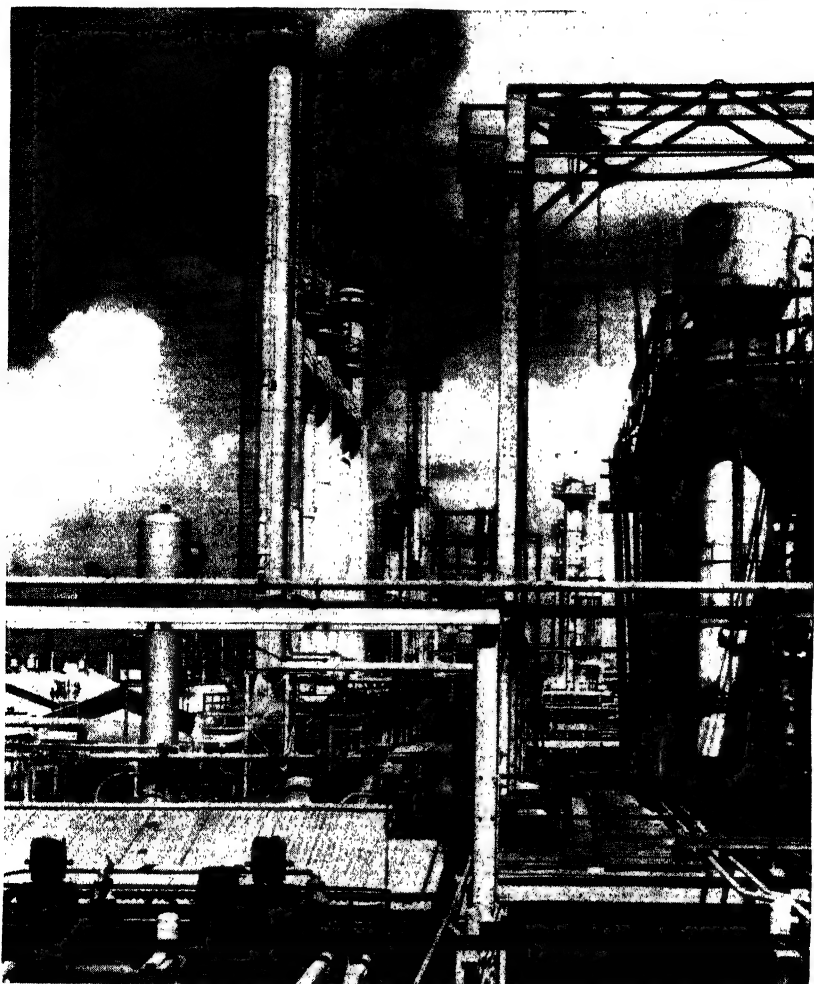
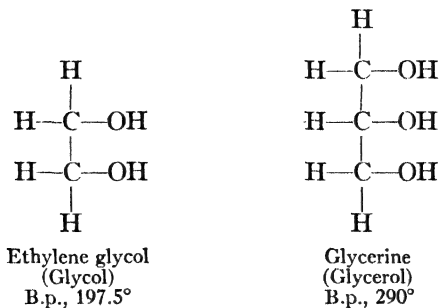


Figure 179. Plant for the production of isopropyl alcohol and *secondary* butyl alcohol from petroleum. (Courtesy of the Shell Chemical Corporation.)

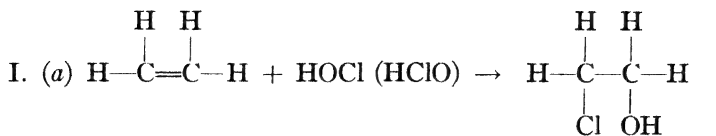


Figure 180. Fermenters used for the production of alcohols by fermentation.
(Courtesy of the Commercial Solvents Corp.)

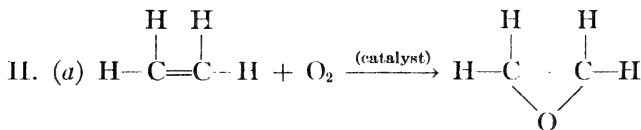
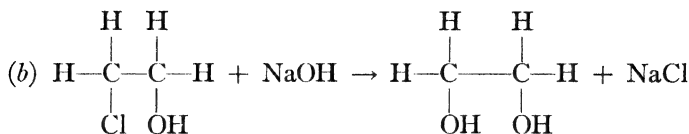
It is also possible to replace more than one hydrogen with a hydroxyl group to give polyhydroxy compounds. The following two compounds of this type are the most important:



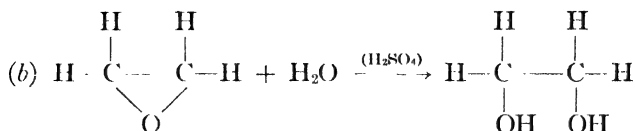
Glycol is made from ethylene by the two methods illustrated by the following equations:



Hypochlorous acid Ethylene chlorohydrin

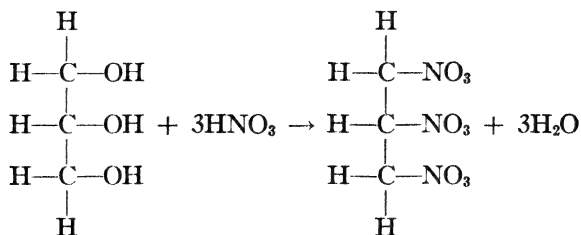


Ethylene oxide



Ethylene glycol is the principal antifreeze of the permanent type, and this use alone accounts for nearly one-half of the 210 million pounds produced each year. It is useful for this purpose because it is completely water-soluble and lowers the freezing point of the water, and because of its high boiling point it will not evaporate as will methyl and isopropyl alcohols. Ethylene glycol and its derivatives are also used as solvents and plasticizers in the paint and varnish industry (Chapter 32). Glycerine is a versatile compound with about 1600 different uses; the most important of these are indicated in Fig. 181.

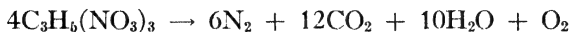
The use of glycerine in the manufacture of explosives is dependent upon the formation of a nitrate by reaction with nitric acid.



Glyceryl trinitrate
(Nitroglycerine)

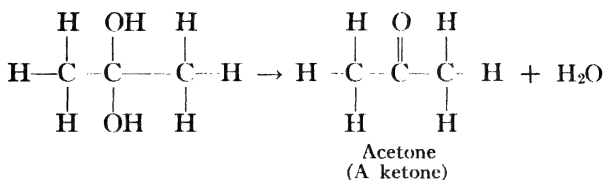
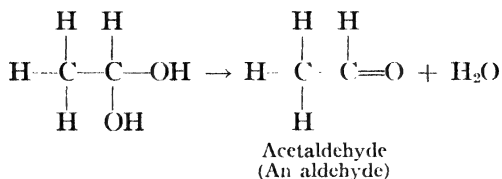
Ethylene glycol will react in a similar manner to form an explosive dinitrate. Both nitrates are used in the preparation of dynamite, a mixture of kieselguhr (a diatomaceous earth), sawdust or charcoal, and nitroglycerine and a smaller amount of glycol dinitrate. Dynamite may also contain some sodium or ammonium nitrate.

The destructiveness of nitroglycerine is the result of the sudden liberation of a very large volume of gas when the compound is irritated.



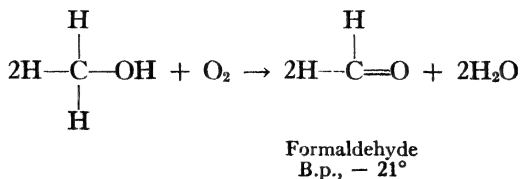
Most explosives are unstable compounds that will decompose when subjected to shock to liberate a large amount of heat and gas.

Aldehydes and Ketones. When two hydrogen atoms on the same carbon atom of a compound are replaced by hydroxyl groups, the resulting compound is unstable. A molecule of water splits off, leaving an aldehyde or ketone, depending on whether or not the carbon atom is terminal. The following equations illustrate this reaction.



Both aldehydes and ketones are made by the oxidation of the appropriate alcohol or hydrocarbon or by the dehydrogenation of an alcohol by use of a catalyst.

Formaldehyde is made by passing vapors of methyl alcohol over a silver or copper catalyst at 250 to 350°C.



Formaldehyde is used in the manufacture of resins (Chapter 32) and other chemicals. A 40 per cent solution of formaldehyde in water (Formalin) is used for preserving anatomical specimens. The practical application of formaldehyde is well-nigh inescapable. The mortician's penultimate service to the deceased employs formaldehyde; it is an

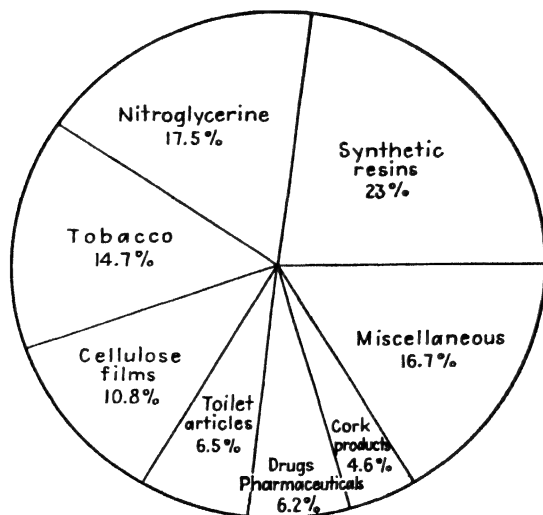
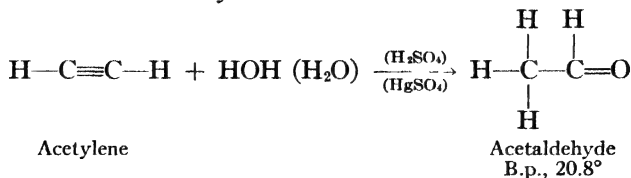


Figure 181. Consumption of glycerine by-products for a typical year

active ingredient in embalming fluids. Approximately 200 million pounds of formaldehyde is produced each year.

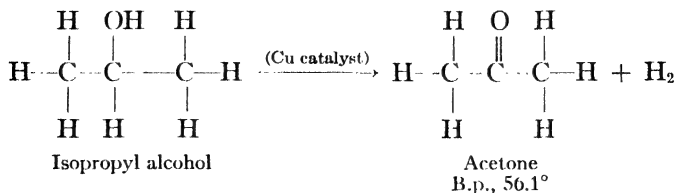
Acetaldehyde may be made from ethyl alcohol by either oxidation or dehydrogenation, but it is more economical to make it from acetylene by the direct addition of water in the presence of sulfuric acid and mercuric sulfate as a catalyst.



Acetaldehyde is used in the synthesis of several compounds (acetic acid, acetic anhydride, ethyl acetate) discussed in the next chapter.

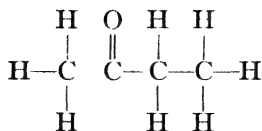
Both aldehydes and ketones are also produced by the direct oxidation of a propane-butane mixture.

Acetone is the simplest ketone and is produced by either oxidation or dehydrogenation of isopropyl alcohol.



Acetone is used extensively as a solvent and to a lesser extent for the production of other compounds.

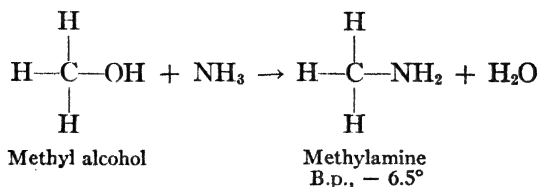
The next higher member of the homologous series, *methyl ethyl ketone* (**MEK**),



is made in a similar manner from *secondary* butyl alcohol and is used as a solvent. It is one of the main solvents used in nail polish and nail-polish remover.

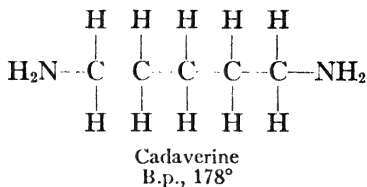
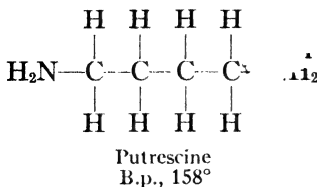
The oxygen atom in aldehydes and ketones is joined to the carbon atom by two pairs of electrons, and these compounds undergo a number of addition reactions in a manner similar to that of the olefins. Because of the nature of the oxygen atom, however, different reagents react than those which add to olefins.

Amines. Amines are organic compounds of ammonia where one, two, or three of the hydrogen atoms of ammonia have been replaced by an organic radical. They may be synthesized by treating ammonia with the corresponding alcohol (with a catalyst) or alkyl halide.



The remaining hydrogen atoms may also be replaced to give dimethylamine and trimethylamine.

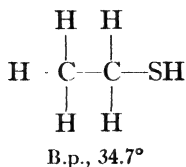
Compounds of this type have an ammonia-like odor but one less pungent and more fish-like. They occur in nature and give dead fish, herring brine, and old sugar-beet pulp their character. Two diamines



are formed in considerable quantities when meat putrefies. They have a disagreeable odor and are poisonous.

Amines are basic in reaction and nearly all their uses are dependent upon this fact. They are the organic bases.

Mercaptans. The mercaptans are sulfur compounds analogous to the alcohols but with the oxygen atom replaced by a sulfur atom. They are produced in the refining of crude oil and occur in nature to a small extent. The most distinguishing feature of these compounds is their onion- or garlic-like odor. Ethyl mercaptan,

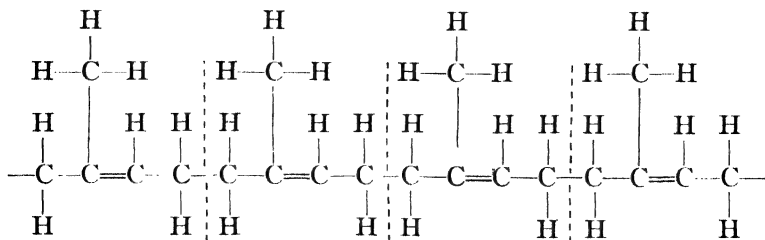


is used as a warning agent in odorless poisonous gases because of its alliaceous odor, which can be detected in a dilution of 1 part in 50 billion parts of air. *Butyl mercaptan* is present in the defensive secretion of the skunk. The active ingredients in onions, garlic, and mustard are rather complex sulfur compounds.

RUBBER

Natural rubber is composed of high-molecular-weight unsaturated hydrocarbons that occur in the coagulated latex of certain tropical trees. The hydrocarbons are made up of isoprene units that have

joined together (polymerized) in the following manner to form very large molecules containing about 100 of these isoprene units:



Pure rubber becomes sticky at body temperature and loses its elasticity if cooled to 0°. The properties of pure rubber are improved by



Figure 182. Rev. Julius Arthur Nieuwland, C.S.C., who pioneered in the production of chloroprene. (Courtesy of *The Edgar Fahs Smith Memorial Collection in the History of Chemistry, The University of Pennsylvania*).

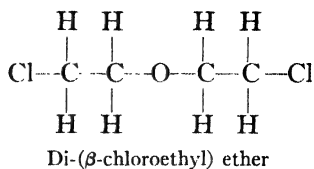
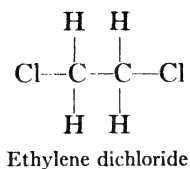
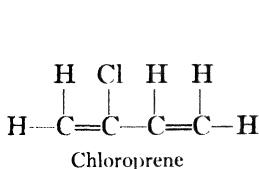
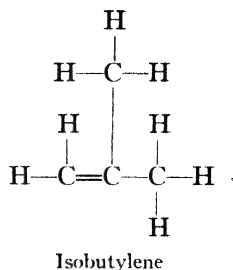
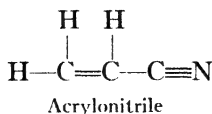
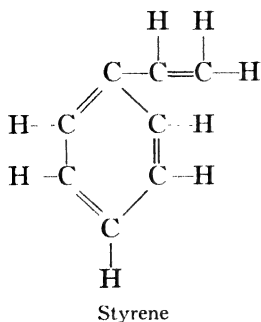
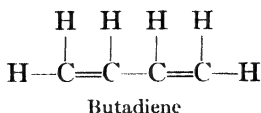
heating it with sulfur (vulcanization) - a typical soft rubber may contain about 5 per cent sulfur, while a hard rubber may contain as much as 30 per cent sulfur. Because rubber is unsaturated, it will also react with atmospheric oxygen and deteriorate rapidly. To prolong the life of the rubber, antioxidants (inhibitors) are added; as little as 1 to 3 per cent of antioxidant greatly prolongs the life of an automobile tire.

Synthetic rubber is the term used for synthetic rubber-like materials, or elastoplastics, which can compete with natural rubber in its many uses, especially for the manufacture of automobile tires, the single largest use of rubber. There was a remarkable develop-

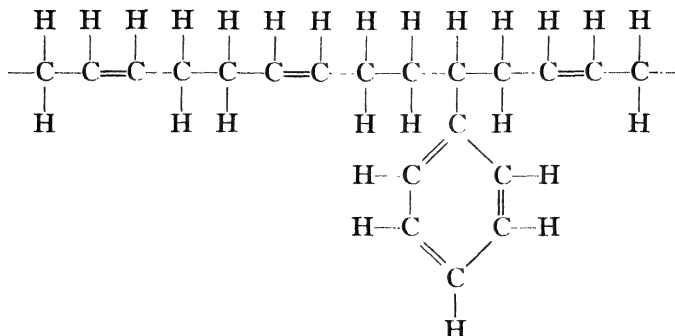
ment of a number of these rubber substitutes during World War II, when all the warring nations with the exception of Japan were without sources of natural rubber. None of these substitutes is a duplicate of natural rubber, and hence the term "synthetic rubber" is mislead-

ing, but because of its wide acceptance it will be used here. It is not necessary even to approximate the structure of natural rubber to produce rubber-like materials.

The following compounds are those most frequently used to produce synthetic rubber:



Butadiene is by far the most important of these compounds. It can be caused to react with itself or with a co-present compound such as styrene or acrylonitrile. The product of the reaction between butadiene molecules does not have desirable properties; but when about 25 per cent of styrene is added, the resultant synthetic rubber (**GR-S**) is at least as good as natural rubber for tire treads and mechanical rubber goods. The styrene is actually incorporated in the molecules of rubber during the process of co-polymerization.



The peak production of rubber of this type was in 1945 and 1946, when over 800,000 tons was produced annually. Acrylonitrile (25 per cent) and butadiene (75 per cent) produce a rubber that shows good resistance to chemicals, oils, aging, and abrasion. This rubber is not produced in large quantities and is not used for tires.

Chloroprene, which closely resembles isoprene, will polymerize by itself to produce a rubber (Neoprene—**GR-M**) that has good resistance to oils and hydrocarbon solvents. It was the first synthetic rubber produced in the United States (1931). Isobutylene polymerizes with a small amount of butadiene to give a rubber noted for its resistance to aging and chemical action. About 80,000 tons of this *butyl rubber* (Vistanex, Polybutene) is produced annually, and most of it is used for inner tubes because of its high air retention.

Both ethylene dichloride and di-(β -chloroethyl) ether will react with sodium polysulfide (Na_2S_x) to form synthetic rubbers known as Thiokols. They are especially resistant to swelling by solvents and to abrasives.

In 1947 the United States consumed 1,200,000 long tons of rubber, of which 50 per cent was natural rubber and 50 per cent synthetic rubber. This compares with 27 per cent natural rubber in 1946 and 13 per cent natural rubber in 1945. The future of synthetic rubber depends upon many factors, not the least being the price of natural rubber, which in 1947 was about 15¢ per pound compared with **GR-S** rubber at 18.5¢ per pound. For special purposes synthetic rubbers will maintain their position; for automobile tires natural rubber is regaining its position lost during World War II. In 1947 over 100,000,000 automobile tires were produced.

EXERCISES

1. *New terms*: synthetic aliphatic chemicals, alkyl halides, alcohols, alcohol, industrial alcohol, denatured alcohol, aldehydes, ketones, amines, mercaptans, vulcanization, polymerization, synthetic rubber, elastoplastics.
2. Suggest an important use for each of the following compounds: (a) pentyl mercaptan, (b) methyl isobutyl ketone, (c) pentyl alcohol, (d) acetaldehyde.
3. Give two general uses of alcohols.
4. Write the formula for (a) dimethylamine; (b) trimethylamine; (c) butyl mercaptan; (d) ethylene dichloride.
5. Give two reasons why dichlorodifluoromethane (Freon-12) is a good compound to use as a refrigerant.
6. Name two compounds that are used with tetraethyl lead in ethyl gasoline.
7. Write an equation illustrating the preparation of ether from alcohol.
8. Why is the term "synthetic rubber" misleading?
9. What type of organic compound would one use to remove acid gases from gaseous mixtures?
10. Name the three classes of foods, and give a specific example of each.
11. What is the principal raw material for the synthetic aliphatic chemical industry?
12. What is the difference between "food" and "feed"?
13. Name four compounds used as antifreezes, and indicate which are of the "permanent" type and which are of the "non-permanent" type.
14. What is considered by some to be the oldest profession?
15. Discuss the place of synthetic rubber in our economy.
16. Calculate the amount of methyl alcohol used each year to produce the normal yearly production of formaldehyde. Assume a 100 per cent yield.

COLLATERAL READING

CONANT and BLATT: "The Chemistry of Organic Compounds," The Macmillan Company, New York, 1947, Chapters 1, 2, 6, 7, 9, and 18.

- FIESER and FIESER: "Organic Chemistry" (abridged), D. C. Heath and Company, Boston, 1944, Chapters 6, 7, 9, 10, and 13.
- MARCHIONNA: "Butalastic Polymers: Their Preparation and Applications," Reinhold Publishing Corporation, New York, 1946.
- MONCRIEFF: "The Chemical Senses," John Wiley & Sons, Inc., New York, 1946.
- READ: "Industrial Chemistry," John Wiley & Sons, Inc., New York, 1943, Chapters 1-4.
- WILLIAMS and HATCH: "Introduction to Organic Chemistry," D. Van Nostrand Company, Inc., New York, 1948, Chapters 3, 5, 6, 7, 11, 13, and 22.

Organic Acids, Esters, Fats, and Soap

MANY materials, such as lemons, sour milk, vinegar, and green apples, have a sour taste, and because of this it may be assumed that these materials contain acids. Some of the earliest research in organic chemistry was carried out to isolate and characterize these compounds. Pasteur added greatly to his reputation (at least with wine-makers) by his work on tartaric acid, an organic acid associated with the souring of wine.

These organic acids all have the characteristics associated with compounds that furnish hydrogen ions to a water solution, and in addition they have the ability to react with alcohols to form *esters* in a manner somewhat similar to the formation of a salt by the reaction between an acid and a base. Esters occur in nature to a small extent and are responsible for most of the odor and flavor of fruits, and to a lesser extent they contribute to the odor of flowers. Fats and oils (vegetable and animal oils) are esters that serve as a food and as a raw material for the manufacture of soap.

Organic acids are important both because of their acidic properties and because of the esters that can be formed from them; esters are used extensively as solvents and to a lesser extent as flavoring agents. Both acids and esters are obtained from natural sources, and they are also synthesized from various raw materials. They are not produced in as large amounts as are some of the types of compounds discussed in the preceding chapter. The relative amounts of the most important types of synthetic aliphatic chemicals that are produced industrially are indicated in Fig. 183. These data do not include fats and oils, of which about 10 billion pounds is used annually in the United States.

Acids. Organic acids may be considered as derivatives of paraffin hydrocarbons in which all three hydrogen atoms on a terminal carbon

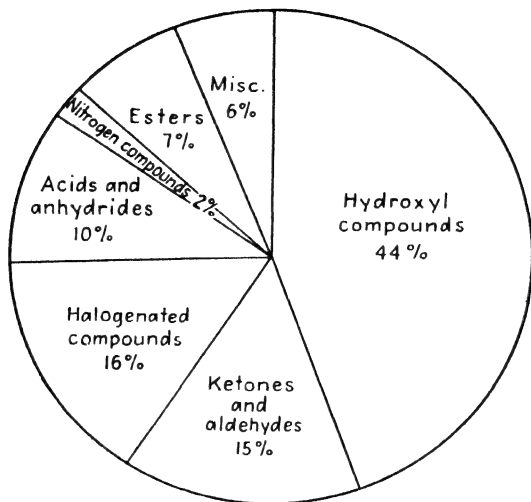
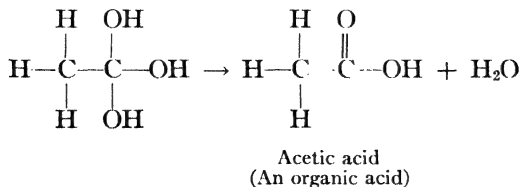
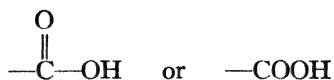


Figure 183. The relative amounts of synthetic and non-synthetic aliphatic compounds, by families, produced in 1945. Hydrocarbons are excluded. [From *Chemical and Engineering News*, **25**, 3210 (1947).]

atom have been replaced by hydroxyl groups. The resulting trihydroxy compound is not stable, and a molecule of water splits off, leaving a double-bonded oxygen atom and a hydroxyl group.

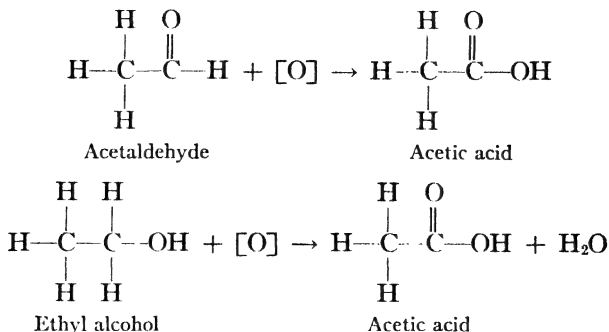


The type formula of an acid is $\text{C}_n\text{H}_{2n+1}\text{COOH}$, and all acids are characterized by containing in their molecular structure at least one *carboxyl group*



The more frequently encountered acids are usually known by common names based upon some special source in nature.

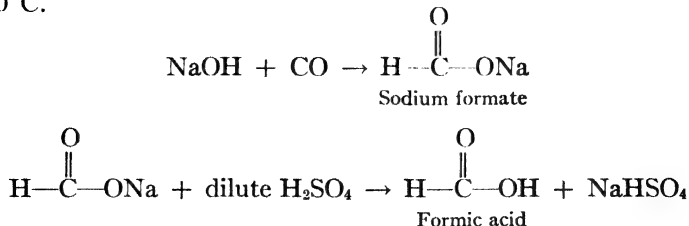
Organic acids are commonly prepared by oxidizing the corresponding aldehyde or alcohol.



These acids have the general characteristics of inorganic acids: in dilute water solutions they will color blue litmus red, evolve hydrogen when acted upon by metals, and neutralize metal hydroxides. The important reaction between alcohols and acids will be noted in the discussion of esters, the product of this type of reaction.

There are relatively few organic acids of importance, and they will be discussed separately because each is prepared by a more or less distinctive method and has specific uses.

Formic acid (Latin *formica*, ant) was so named because it occurs in the bodies of red ants and was first obtained from them by distillation. The irritating effect of many insect (ant) bites and plant (nettle) stings is due in part to the injection of formic acid under the skin. Formic acid is produced commercially by the reaction between carbon monoxide (from water gas) and pulverized sodium hydroxide at 120 to 150°C.



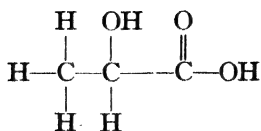
Formic acid is a strong acid and is used in the textile and rubber industries as an inexpensive acidifying agent. Because it also has a strong bactericidal action, it is used in disinfecting wine casks. Most of its uses, however, are dependent upon its being of strongly acidic character.

Acetic acid is the most important of the organic acids not because of its many direct uses but because it is widely used to make other more useful materials such as rayon, plastics, solvents, and flavoring compounds. Pure acetic acid (*glacial* acetic acid) is made industrially by the air oxidation of ethyl alcohol over a metal catalyst and by the hydration of acetylene followed by oxidation of the resulting acetaldehyde. The Fischer-Tropsch process and direct oxidation of hydrocarbons will also become important in the future as sources of acetic acid.

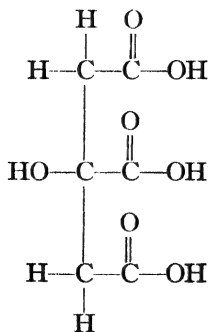
A dilute water solution of acetic acid called *vinegar* is obtained by the fermentation of alcohol-containing solutions such as wine or hard cider. Vinegars produced from fruit juices are known as *cider* vinegars and usually possess an odor characteristic of the fruit from which the vinegar was produced. *Spirit*, or *reduced*, vinegars are made from pure acetic acid and are either colorless or colored brown by the addition of caramel. Vinegar is not a source of concentrated or pure acetic acid.

Many of the acids of higher molecular weight occur in plant and animal products either as the free acid or as the ester of glycerine. *Butyric acid* (C_4) gives rancid butter and stale perspiration their characteristic odors, and caproic (C_6), caprylic (C_8), and capric (C_{10}) acids are known as the goat acids for obvious reasons. Acids having an even number of carbon atoms from C_{12} to C_{18} are found in the form of esters of glycerine in animal and vegetable fats and oils. The aluminum salts of these high-molecular-weight acids are used extensively in the compounding of greases.

Lactic acid, as the name implies, is the acid of sour milk, from which it is obtained, and *citric acid* is the acid of citrus fruits.



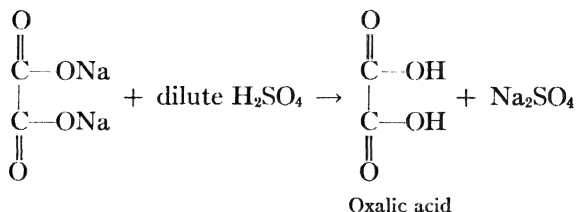
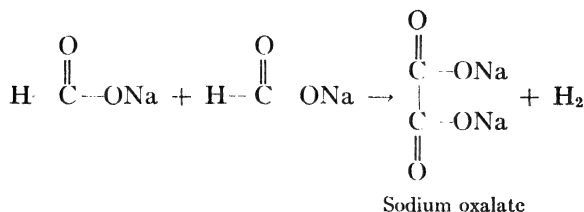
Lactic acid



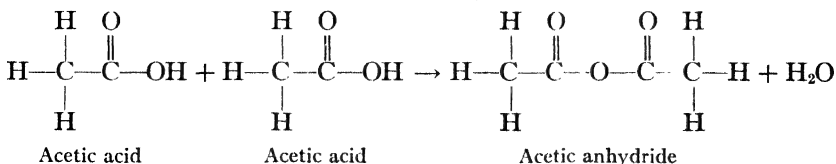
Citric acid

Lactic acid is used in contraceptives and in the preparation of plastics. Citric acid and its magnesium salt (magnesium citrate) are used as laxatives; citric acid is also the most widely used organic acid in the food and beverage industry. One pound of citric acid (40¢), one lemon (5¢), and one barrel of water (1¢) plus a little sugar equals one barrel of lemonade (\$50 retail). Citric acid is made commercially by the fermentation of molasses.

Oxalic acid occurs in the leaves of several plants (*e.g.*, rhubarb) and is very poisonous. It is used by laundries as an acid rinse to remove iron stains and as a bleaching agent for leather and straw goods and for woodwork that has become discolored. Oxalic acid may also be used to remove ink spots, especially those caused by the "permanent" blue-black inks containing iron. It is made industrially by heating sodium formate.

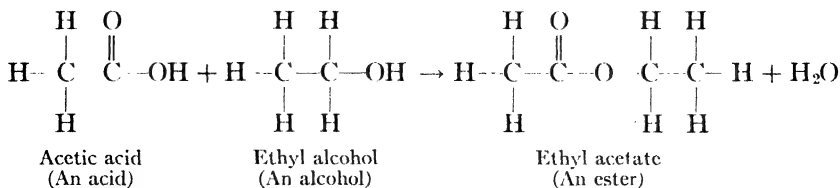
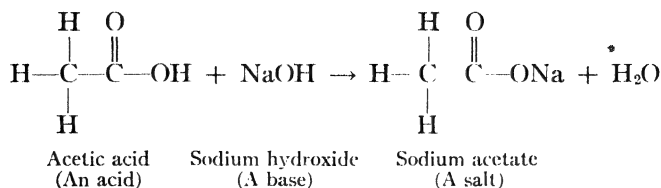


Anhydrides. Two molecules of an acid can react by splitting off a molecule of water to form a type of compound called an *acid anhydride*,



in a manner similar to that of the dehydration of two molecules of an alcohol to form an ether. Acid anhydrides are used to make derivatives of acids.

Esters. The reaction that occurs between an organic acid and an alcohol to give an ester and water (*esterification*) has already been mentioned as one of the most important reactions of both acids and alcohols. The reaction is very similar to that between an acid and a base to form a salt and water, but the ester does not ionize in a water solution and has all the characteristics of an organic compound, which it is.



Acetic acid is the organic acid most frequently used for the production of esters and salts; about 60 million dollars worth of acetates is produced annually. *Ethyl acetate* is the most valuable ester because of its excellent solvent properties and because of its low cost. Esters of the

TABLE 14. Odors and Flavors of Certain Esters

<i>Name of ester</i>	<i>Odor and/or flavor</i>
Isobutyl formate.....	Raspberry
Isobutyl acetate.....	Raspberry
Amyl acetate.....	Banana
Isoamyl acetate.....	Pear
Octyl acetate.....	Orange
Methyl butyrate.....	Pineapple
Butyl butyrate.....	Pineapple
Amyl butyrate.....	Apricot
Isoamyl isovalerate.....	Apple
Ethyl butyrate.....	Rose
Ethyl nonylate.....	Rose
Amyl undecylate.....	Rose
Methyl salicylate.....	Wintergreen
Ethyl formate.....	Rum
Ethyl heptoate.....	Cognac brandy

other acids and alcohols are also used as solvents; and because they are frequently characteristically odoriferous, they are used in compounding artificial flavors, perfumes, etc. Table 14 gives a list of some of the commoner esters and their flavors and odors.

Artificial flavoring essences are mixtures of synthetic esters compounded to reproduce the flavor and aroma of natural fruits and ex-

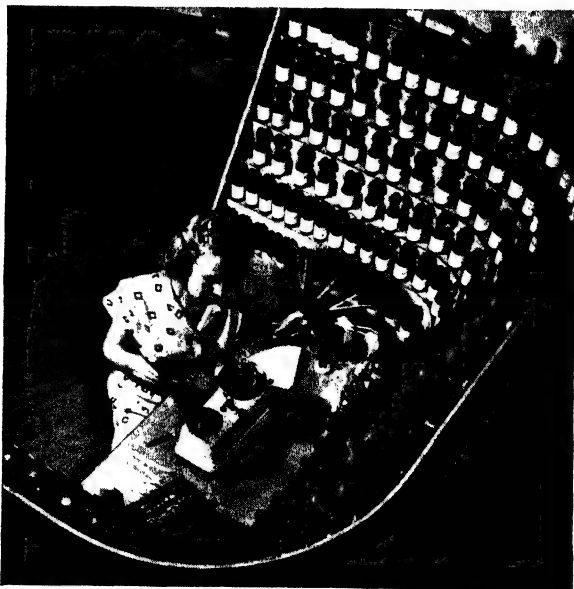


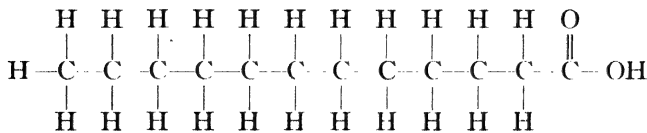
Figure 184. "Perfumer's organ" where new perfumes and flavors are originated. The naming of the perfumes is done elsewhere. (Courtesy of E. I. duPont de Nemours & Co.)

tracts (Fig. 184). These ester mixtures are usually prepared in an alcoholic solution containing glycerine, chloroform, or acetaldehyde as fixatives to retain the fragrant principles. Organic acids (*e.g.*, citric acid) are often added to simulate the tartness of fruits. One formula for artificial raspberry flavor employs nine different esters, two organic acids, acetaldehyde, glycerine, and alcohol.

Fats and Oils. The main esters produced by plants and animals are those complex mixtures of esters called *fats* (or vegetable and animal oils, if liquid). A fat may be defined as a mixture of esters that on hydrolysis yields a mixture of high-molecular-weight organic acids and glycerine. *Hydrolysis* is the term used to describe the reaction between

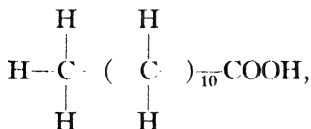
water and an ester to form an acid and an alcohol, just the opposite of ester formation (esterification). The most characteristic feature of fats is that they are always mixtures of esters but of only one alcohol—glycerine. Because this alcohol has three hydroxyl groups in each molecule, there may be one, two, or three different acids forming a single ester molecule.

The principal acids found on hydrolysis of fats are

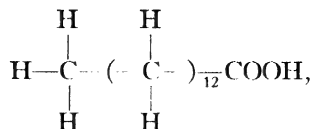


Lauric acid

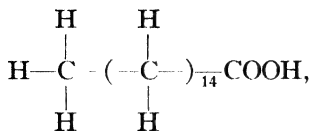
or to conserve space,



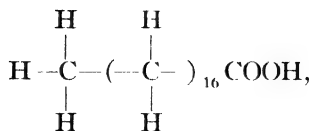
Lauric acid
M.p., 43.6°



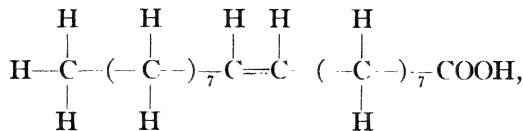
Myristic acid
M.p., 58.0°



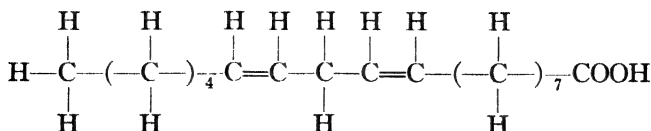
Palmitic acid
M.p., 62.9°



Stearic acid
M.p., 69.9°



Oleic acid
M.p., 13–16°



Linoleic acid
(Liquid)

These acids all contain an even number of carbon atoms, as do nearly all of the other forty some acids found in nature, and it is significant that the human body can utilize completely only acids containing an even number of carbon atoms.

Both saturated and unsaturated acids are present in fats in the form of their glycerine esters. Physiologically it makes little difference whether the fats are unsaturated or not, but it determines the physical state of the fat. The greater the degree of unsaturation, the lower the melting point of the fats. The basic difference between a fat and an oil (vegetable or animal) is in the degree of unsaturation; for example, the saturated stearic acid ester occurs in large amounts in the solid fats of animals but is usually found only in traces in liquid vegetable oils, while olive oil contains about 83 per cent of the unsaturated ester of oleic acid.

The number of different acids resulting from the hydrolysis of a fat will vary, depending upon the fat's antecedents. Some fats will yield only three or four different acids, while butter, one of the more complex fats, involves fourteen acids.¹ Table 15 gives the average percentages of different acids obtained from some of the more common fats.

TABLE 15. Acids Obtained from Fats and Oils*

<i>Fat or oil</i>	<i>Fatty acids, per cent</i>							
	<i>Caprylic</i>	<i>Capric</i>	<i>Lauric</i>	<i>Myristic</i>	<i>Palmitic</i>	<i>Stearic</i>	<i>Oleic</i>	<i>Linoleic</i>
Coconut ..	8.0	7.0	48.0	17.5	8.2	2.0	6.0	2.5
Babassu ..	6.5	2.7	45.8	19.9	6.9	..	18.1	—
Palm kernel ..	3.0	3.0	52.0	15.0	7.5	2.5	16.0	1.0
Palm	1.0	42.5	4.0	43.0	9.5
Olive	6.0	4.0	83.0	7.0
Peanut	7.0	5.0	60.0	21.0
Beef tallow	2.0	32.5	14.5	48.3	2.7
Lard	1.1	30.4	17.9	41.2	5.7

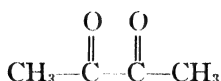
* From data supplied by the Werner G. Smith Company.

The figures given in Table 15 are averages, for the same fat from different localities will vary somewhat in composition. The degree of unsaturation is markedly influenced by the temperature at which formation took place. Linseed oil from seed grown in Switzerland is

¹ Butyric, 3%; caproic, 1.4%; caprylic, 1.5%; capric, 2.7%; lauric, 3.7%; myristic, 12.1%; palmitic, 25.3%; stearic, 9.2%; oleic, 29.6%; linoleic, 3.6%; and 4 other unsaturated acids, 7.3%.

more unsaturated (liquid at a lower temperature) than linseed oil from seed grown in a warmer climate. The character of animal fat is also dependent upon the nature of the fat in the diet of the animal. Lard from corn-fed hogs is more saturated than lard from peanut-fed hogs. The character of human fat can also be varied by diet. Oleic acid is the chief acid of the depot fat of herbivorous animals; mutton and beef tallows contain about 50 per cent oleic acid, and neat's-foot oil from ox hoof contains 80 per cent.

Solid fats are generally preferable to liquid fats for the manufacture of soap and as a food, at least in the United States. This is in some respects unfortunate, for most fats that occur in nature are liquids. This is not an insuperable obstacle, however, because of the relationship between unsaturation and melting point. To make an unsaturated liquid fat (oil) into a saturated solid fat it is necessary only to add hydrogen to the double bonds present in the oil. This addition of hydrogen can be caused to take place at relatively low temperatures and pressures by use of a nickel catalyst (Chapter 10). In this manner cottonseed, soybean, and peanut oils are frequently partly hardened to the consistency of lard and used as shortening (Spry, Crisco, Snow-drift, etc.). If a butter substitute is desired, the hardened oil is churned with a little milk to give it a butter flavor, or diacetyl

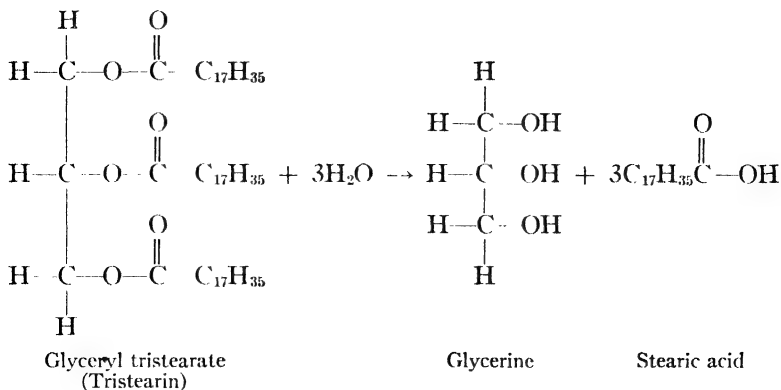


is added because it has the color, odor, and flavor of butter. The *oleomargarines* thus produced are now so skillfully blended and fortified with vitamins that they equal butter in food value and excel butter in uniformity of composition. During certain seasons of the year butter is both artificially colored and flavored the same as oleomargarine.

Of the nearly 10 billion pounds of fats and oils used annually about 6 billion pounds is used as food. Of the remaining 3.8 billion pounds, 2 billion is used to manufacture soap, 1 billion is used for drying oils, and 140 million for lubricants. The remaining 650 million pounds is used in miscellaneous manufactured products such as rubber, leather, plastics, candles, cosmetics, tin plating, etc. *Drying oils* are highly unsaturated fats (linseed oil, tung oil, etc.) which react with the oxygen of the air to form a hard, tough, horn-like substance. They are used in paint and varnish (Chapter 32).

The United States is self-sufficient in the production of edible fats, but for industrial needs we must import coconut, palm, linseed, rapeseed, and castor oils.

Soap. The metal salts of the high-molecular-weight organic acids that occur as esters in fats are called *soaps*. The sodium salts are the most widely used soaps because they are less expensive and more generally useful. The older method of soap manufacture consisted in heating natural or hardened fats with sodium hydroxide in an open kettle until the alkaline hydrolysis (*saponification*) of the ester was complete with the formation of the sodium salts of the acids and with glycerine as a by-product. Recently there has been an important change from this and similar batch processes to a continuous process wherein crude fats are hydrolyzed by water under pressure of about 700 pounds at a temperature of 200°C. (Fig. 185.)



The acids obtained by this process are neutralized by sodium carbonate, which costs about half as much as sodium hydroxide. The soap is then precipitated by the addition of salt, and the crude soap thus obtained contains glycerine, alkali, and salt as impurities. These impurities are removed by boiling the mixture with sufficient water to form a homogeneous liquid from which the soap is reprecipitated by the addition of more salt. Several reprecipitations are necessary to obtain the soap of commerce called *kettle soap*, which consists of 69 to 70 per cent soap, 30 per cent water, and 0.2 to 0.5 per cent salt. *Toilet soaps* are made from kettle soap that has been dried to contain 85 to

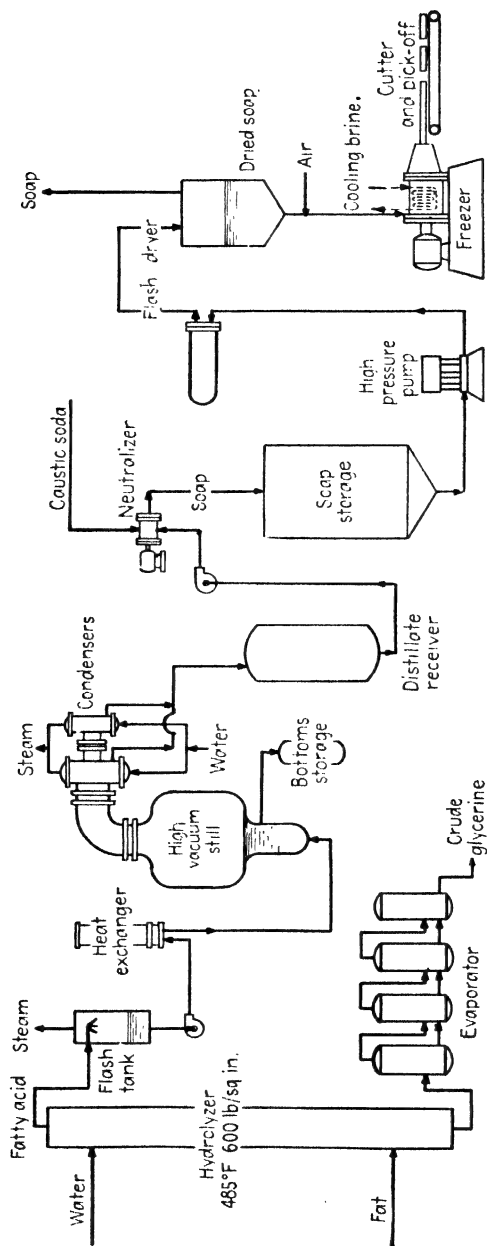


Figure 185. Flow chart showing the continuous production of soap. (Courtesy of The Procter & Gamble Company.)

90 per cent soap, milled with perfume to thin shavings, and compressed into bars.

It should be apparent by this time that toilet soap is a complex mixture of the sodium salts of several different acids and contains 10 to 15 per cent water plus perfume and in some cases an added color. When one adds to this the fact that many different brands of soap are made from the same batch of kettle soap, one may be justly suspicious of some of the advertising claims that are made. The modern "soap opera" so familiar in radio advertising is the vehicle for an obnoxious sales practice characterized by flatulent claims having little if any basis in fact. These products are advertised in terms of platitudes and generalities that upon careful examination may be shown to be evasive and substantially meaningless. What does it mean, for example, to claim that a given soap is "better than any other soap tested" unless one specifies the identity of the other soaps and the methods whereby the tests were conducted? It is claimed that one brand of soap will make one more glamorous; another is supposed to make one more acceptable socially, but in this latter case one may rightfully wonder whether the cure is not more offensive than the ailment. Any commercial product that is sold on the basis of an appeal to the emotions is usually very similar to its competitors. In the same price range, soap is soap, and only hucksters can tell the difference (if any).

There are a number of soaps prepared for special uses. Scouring soaps have had sand, pumice, or similar material added to secure the

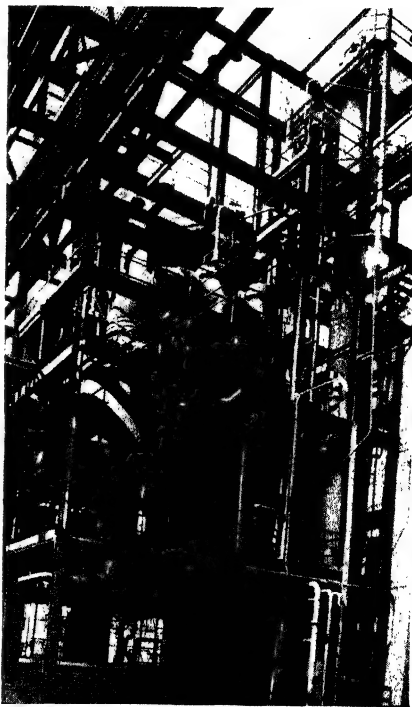


Figure 186. Hydrolyzer and high-vacuum still for the continuous production of soap. (Courtesy of The Proctor & Gamble Company.)

abrasive action. Medicated soaps and soaps that smell like sheep-dip have had antiseptics added (Chapter 30). The household washing powders are made from kettle soap to which has been added sodium silicate or sodium carbonate and an emulsifying agent such as tetra-sodium pyrophosphate; the resulting hot liquid mixture is spray-dried. Potassium soaps are softer and are used in shaving creams, liquid soaps, etc.

The specific gravity of ordinary soaps is slightly greater than that of

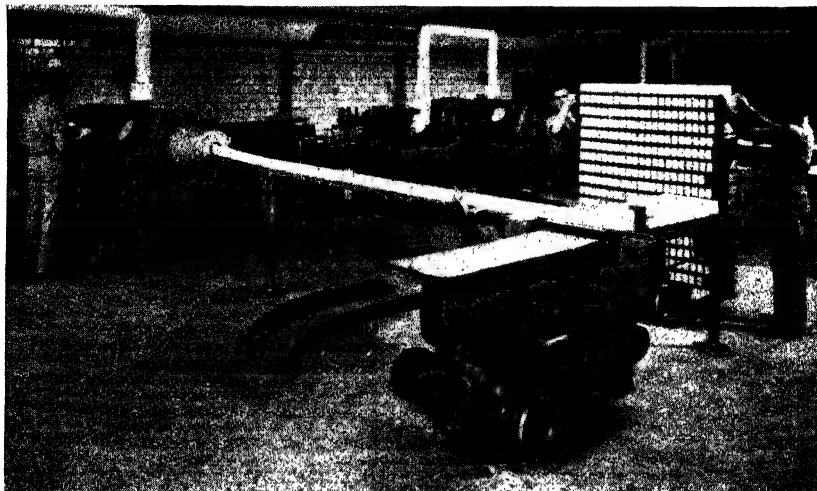


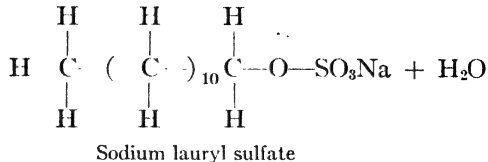
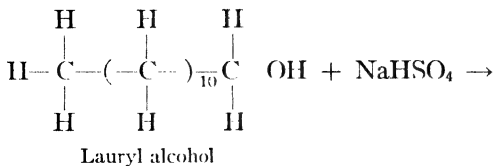
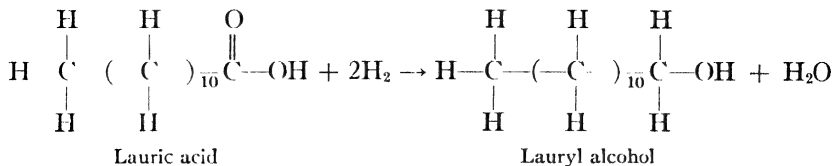
Figure 187. Soap extruded in strip form, cut into three-bar lengths, and stacked for cooling. (Courtesy of The Procter & Gamble Company.)

water, and hence they will not float. When air is blown into the dried soap chips at an elevated temperature and the mass extruded, the resultant soap has a specific gravity less than that of water and will float. Such soap is not necessarily more pure than other soap; it just contains more air.

Tallow is the most important fat for the production of soap, although coconut, babassu, and palm-kernel oils are widely used in conjunction with tallow. About 2.6 billion pounds of soap with a value of half a billion dollars is produced annually.

Synthetic Detergents. Soap is the most widely used detergent, but it has certain limitations such as its instability in acid solutions and its ability to form insoluble salts with the calcium and magnesium com-

pounds usually present in hard water (Chapter 12). The first synthetic compounds to compete with soap were developed about 1860 and were formed by treating castor oil with concentrated sulfuric acid. It was not until about 1930, however, that really successful synthetic detergents were produced on a large scale. These compounds were the sulfates of long-chain alcohols prepared by the hydrogenation of fats (coconut, babassu, or palm-kernel oil).



This and similar sodium alkyl sulfates are sold under various trade names (Gardinol, Dreft, Drene, Modinal, Irium, etc.). They are stable in acid solutions and do not form insoluble salts in hard water.

There are now produced in this country over two hundred different synthetic detergents. The production of these detergents has increased from 65 million pounds in 1939 to over 700 million pounds in 1947 with the industry maintaining this rapid rate of expansion. Nearly half of these detergents come from petroleum and the remainder from sulfonated fats and oils.

Waxes. Waxes are the esters of high-molecular-weight organic acids, but they differ from fats in that they are esters of high-molecular-weight monohydroxy alcohols and sterols (complex alcohols) instead of being esters of glycerine. The alcohols contain an even number of carbon atoms and usually have 16 to 36 carbon atoms per molecule; the acids

are also even-numbered and have a carbon content of 24 to 36. Because of the complexity of the mixtures, little is known about the chemical composition of the waxes.

EXERCISES

1. *New terms:* ester, fat, carboxyl group, animal and vegetable oils, glacial acetic acid, vinegar, cider vinegar, reduced vinegar, acid anhydride, esterification, oleomargarine, drying oils, saponification, wax, kettle soap, toilet soap, synthetic detergents.
2. List ten substances, naturally occurring or produced commercially, that have a sour taste owing to the presence of organic acids.
3. What simple experiment would give good evidence that acids are responsible for the sour taste in a naturally occurring substance?
4. If one wished to put on a few pounds of solid fat, would it be better to eat a quantity of coconut meat or olive oil? Explain.
5. Write an equation illustrating the preparation of soap directly from a fat (use tristearin as the fat).
6. Why would vinegar not be a good source of pure acetic acid?
7. What is the basic chemical difference between a vegetable oil and a solid animal fat?
8. Why is acetic acid the most widely used acid for the production of esters?
9. The taste and odor of rancid butter are caused by the presence of butyric acid. How may one easily remove this taste and odor?
10. What is the basic chemical difference between a wax and a fat?
11. Why not use concentrated sulfuric acid instead of dilute sulfuric acid in obtaining the free organic acid from one of its salts?
12. What is the etymology of the names of the following acids: (a) caproic; (b) formic; (c) citric; (d) oxalic; (e) lactic?
13. List several ways in which organic acids resemble inorganic acids.
14. List several ways in which organic acids differ from inorganic acids.
15. From the standpoint of chemistry, household ammonia would be useful in the treatment of the bite of a red ant. Write an equation illustrating the chemical reaction involved.

16. Write equations representing the following indicated reactions:
 - a. The commercial production of formic acid
 - b. The preparation of sodium lauryl sulfate from lauric acid
 - c. The preparation of acetic acid from acetylene
 - d. The preparation of ethyl butyrate
17. Calculate the number of pounds of soap produced annually in the United States for every man, woman, and child (assume a population of 145,000,000).
18. What is the average per capita yearly consumption of edible oils in the United States?

COLLATERAL READING

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Chemicals from Coal.

Explosives. Dyes

ALTHOUGH justifiable emphasis has been placed in the preceding chapters on petroleum as a storehouse of chemicals, it was not until about 1930 that it gained this eminence. Until that time the history of synthetic organic chemistry was the history of the chemicals from coal, and coal still is a very important source. These chemicals are obtained as a by-product when coal is heated in the absence of air to form coke (Fig. 155).

Before World War I the United States imported most of her organic chemicals from Germany, but the necessity of producing these compounds was forced upon her during that war by the British blockade of Germany. Until then the coke industry in this country had used the chemical by-products of coke manufacture only as a fuel. An indirect result of World War I, therefore, was the birth of the synthetic-chemical industry in the United States.

Table 16 gives a list of the more important chemicals obtained from coal. This list is not impressive from the standpoint of quantity, but what it lacks in quantity it more than makes up for in quality, as will be indicated in this and subsequent chapters. These compounds are all related to benzene and are aromatic compounds. Aromatic hydrocarbons are more reactive toward reagents such as sulfuric acid and nitric acid than are the paraffin hydrocarbons, and many different derivatives may be made from a relatively few compounds. These hydrocarbons and their more important reactions are the subject of the remainder of this chapter. They are used in the production of perfumes, medicinals, dyes, explosives, plastics, agricultural chemicals, and many other organic materials.

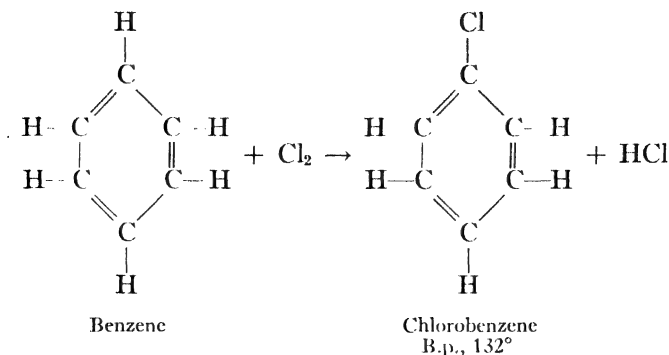
TABLE 16. Products from the Distillation of Coal
(Individual compounds and principal fractions)

<i>Fraction (quantity per ton of coal)</i>	<i>Compounds and fractions</i>	<i>1947 production</i>
Coke-oven gas (11,200 cu. ft.)	Hydrogen (52%) Methane (32%) Carbon monoxide (4-9%) Carbon dioxide (2%) Nitrogen (4-5%) Ethylene and other olefins (3-4%)	
Ammonia (5.5 lb.)	In the form of ammonium sulfate In the form of ammonia water	1,641,041,000 lb. 51,429,000 lb.
Light oil (2.85 gal.)	Benzene (65%) Toluene (15%) Xylenes (7%) Light solvent naphtha (10%)	160,126,000 gal. 27,354,000 gal. 7,216,000 gal. 597,000 gal.
Coal tar (150 lb.)	Naphthalene (11%) Pyridine Heavy solvent naphtha Cresote oil (phenol, cresols, etc.) Total crude coal tar	96,664,000 lb. 787,000 gal. 4,426,000 gal. 39,299,000 gal. 736,351,000 gal.
Coke (1400 lb.)		145,893,344,000 lb.

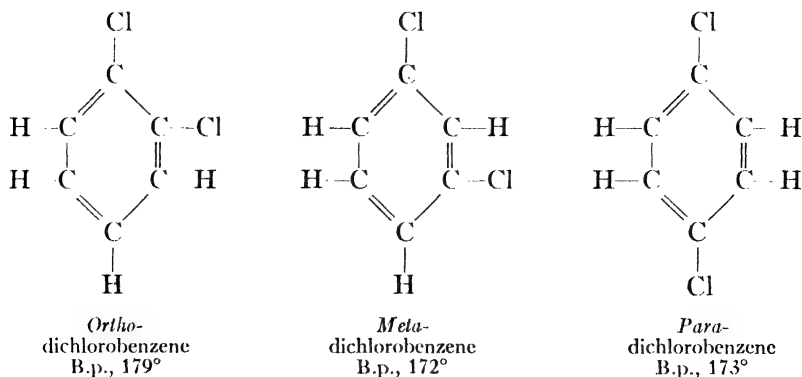
As the chemical industries expand and the demand for aromatic chemicals increases, the supply from coal will remain constant because these chemicals are by-products, with their rate of production set by the production of coke and steel (Chapter 21). Petroleum, however, is now in a position to furnish the three most important hydrocarbons, benzene, toluene, and naphthalene. Toluene and naphthalene derivatives are already being based on petroleum, benzene derivatives soon will be, and it is conceivable that in the future petroleum will become the principal source of these products.

Aromatic Hydrocarbons. *Benzene* is considered the parent aromatic hydrocarbon and also the most important and in some respects the most typical of the aromatic hydrocarbons. It is used as a motor fuel, solvent, and dry cleaner, to produce nylon intermediates, detergents, styrene for synthetic rubber, and in the synthesis of other valuable compounds. Its wide use in synthesis is the result of its ability to undergo chlorination, nitration, and sulfonation. These reactions are general for aromatic compounds and will be illustrated with benzene.

Benzene will react with chlorine (*chlorination*) in the presence of iron as a catalyst to produce *chlorobenzene*.



Because of the presence of other hydrogen atoms in the chlorobenzene molecule it would be anticipated that a dichlorobenzene would be produced if more chlorine were used. This raises the question as to the position of the second chlorine atom in respect to the first chlorine atom. There are actually three isomers of dichlorobenzene, each with different physical and, to some extent, chemical properties.



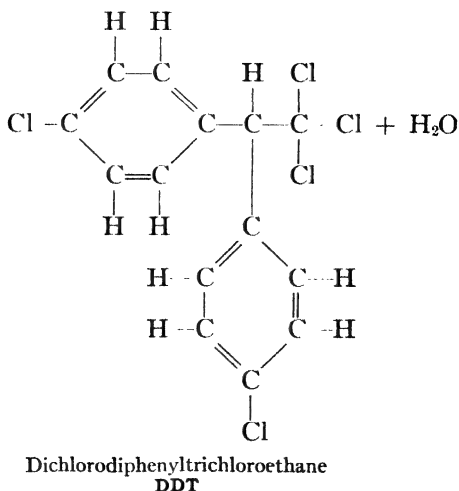
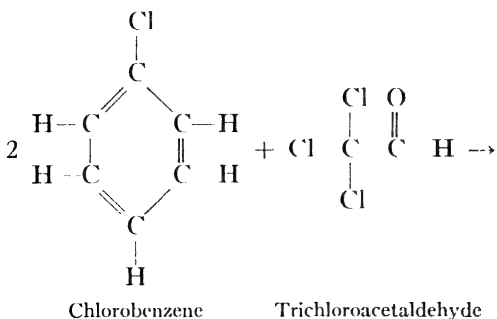
The designations *ortho*, *meta*, and *para* are used whenever there are two hydrogen atoms on a benzene ring replaced by another atom or group of atoms. *Ortho* (*o*) is used when the substitution has occurred on adjacent atoms; *meta* (*m*) is used when there is an intervening

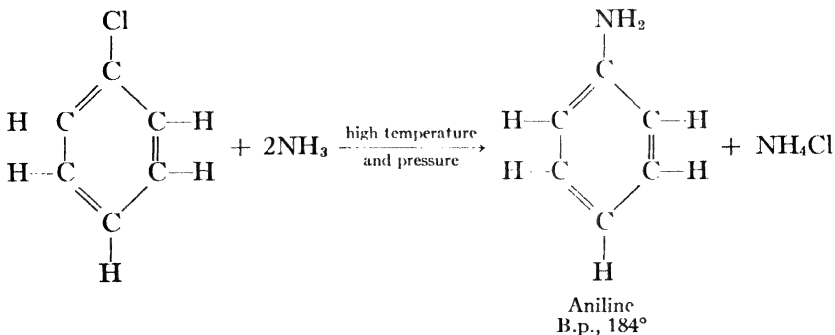
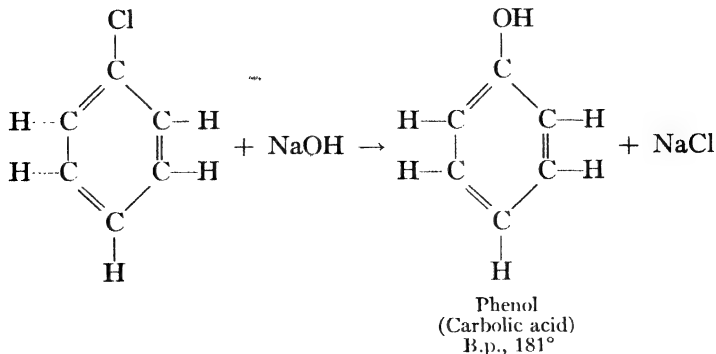
carbon atom; and *para* (*p*), when the substituents are opposite one another on the benzene ring.

With chlorine, only the *ortho*- and *para*-dichlorobenzenes are formed; with some other reactants only the *meta* derivatives are formed. The reason for the absence of the *meta* derivatives from some compounds and the formation of only the *meta* derivatives with other compounds has given the chemist much worry.

Para-dichlorobenzene is used extensively as a moth and caterpillar repellent and as a room deodorant. Chlorobenzene itself is used to make **DDT**, phenol, aniline, and many other compounds.

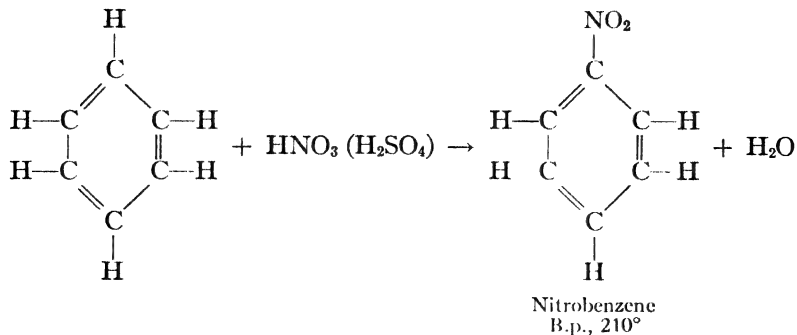
DDT is used as an insecticide (Chapter 31).



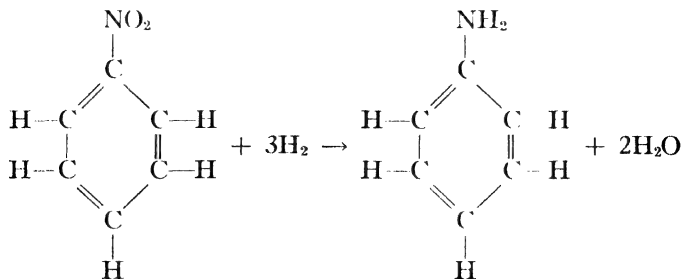


The name *phenol* refers to hydroxybenzene, while the term phenol refers to any aromatic hydroxy compound. Because phenols are used extensively in medicine and pharmaceuticals, they are discussed in Chapter 30. Phenol (*carbolic acid*) resembles the alcohols in structure, but it is distinctly acidic in character. Phenol is used to make phenol-formaldehyde resins (Bakelite) and nylon, and is obtained to some extent from both petroleum and coal. About 75 per cent of the phenol is produced from chlorobenzene and benzenesulfonic acid (see page 445).

Over 100 million pounds of aniline a year is produced from both chlorobenzene and nitrobenzene. Aniline is a highly toxic substance which destroys red blood corpuscles; this action is first manifest when the victim's lips begin to turn blue. *Nitrobenzene* is prepared from benzene by the action of concentrated nitric acid (in the presence of concentrated sulfuric acid to absorb the water formed by the reaction).

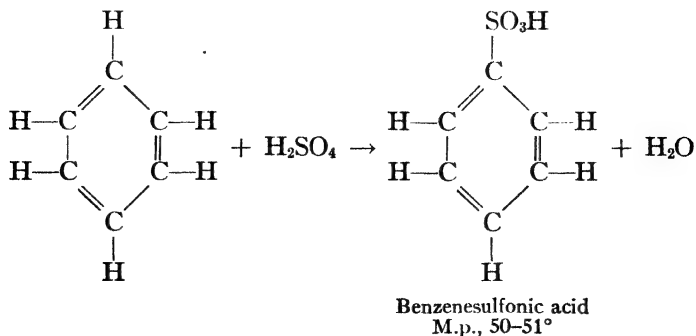


This is a *nitration* reaction, and an excess of nitric acid will give *meta*-dinitrobenzene. Nitrobenzene is used to a small extent as a solvent, but its primary use is in the production of aniline by reaction with hydrogen generated from hydrochloric acid and iron chips.

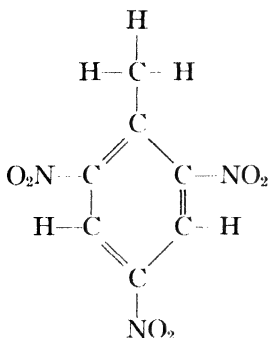


Aniline in turn has very few uses other than to produce other compounds, many of which are dyes and medicinals.

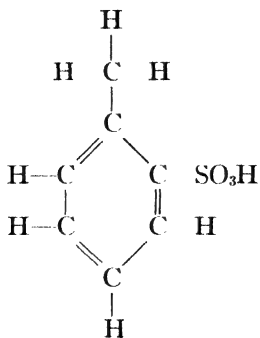
The reaction between benzene and concentrated sulfuric acid (a reaction of the type known as *sulfonation*) yields *benzenesulfonic acid*.



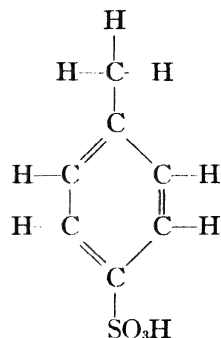
In time of peace, toluene is used as a solvent and diluent by the paint and varnish industry (Chapter 32), as a raw material for the production of other compounds by the chemical industry, and as an additive to improve the quality of gasoline. The usefulness of toluene for the manufacture of explosives is dependent upon its reaction with nitric acid to form *trinitrotoluene* (**TNT**). It will also react with sulfuric acid to form two toluenesulfonic acids.



Trinitrotoluene
TNT



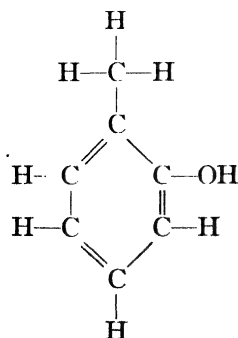
o-Toluenesulfonic acid



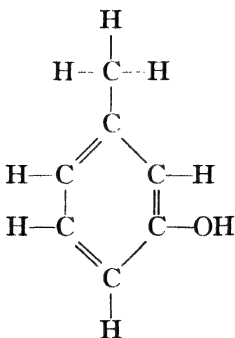
p-Toluenesulfonic acid

o-Toluenesulfonic acid is used in the preparation of saccharin (Chapter 30), and *p*-toluenesulfonic acid is used to prepare various antiseptics (chloramine-T).

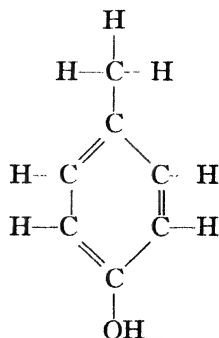
The hydroxy toluenes are called *cresols* and are obtained from both petroleum (35 per cent) and coal (65 per cent). There are three different cresols.



o-Cresol
B.p., 191°



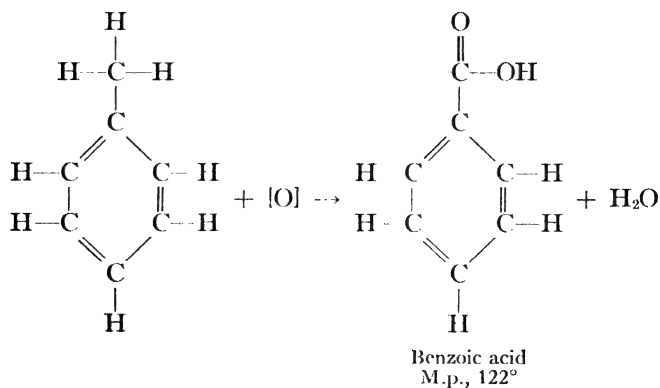
m-Cresol
B.p., 201°



p-Cresol
B.p., 201°

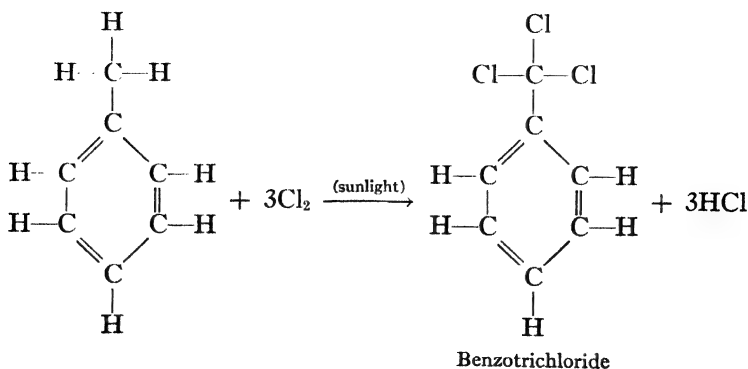
Cresols are used in the refining of lubricating oil (under the name of *cresylic acid*), in certain soaps, and in an antiseptic solution stabilized by soap (Lysol). They are also the main active ingredient of sheep-dip and related materials. Because of their close boiling points it is impractical to separate the cresols, and they are consequently used as the naturally occurring mixtures.

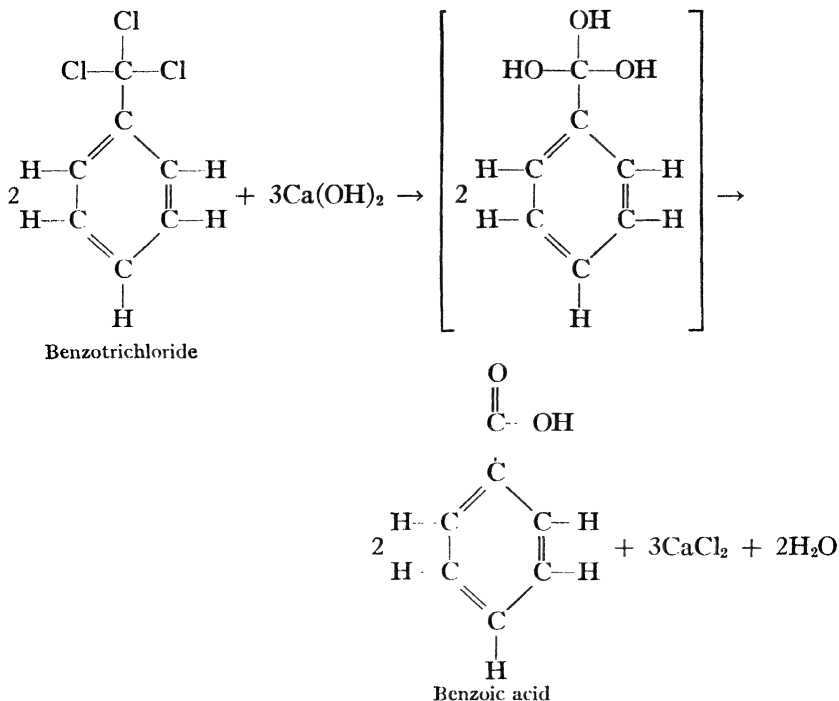
Toluene can be oxidized by chemicals more readily than either paraffin hydrocarbons or benzene. The oxidation takes place on the methyl *side-chain* and produces benzoic acid.



This reaction is typical of any group (*side-chain*) on the benzene ring, regardless of the nature of the group, provided there is a carbon atom attached to the ring.

Benzoic acid is prepared industrially by the chlorination of toluene followed by hydrolysis of the resulting trichloride.

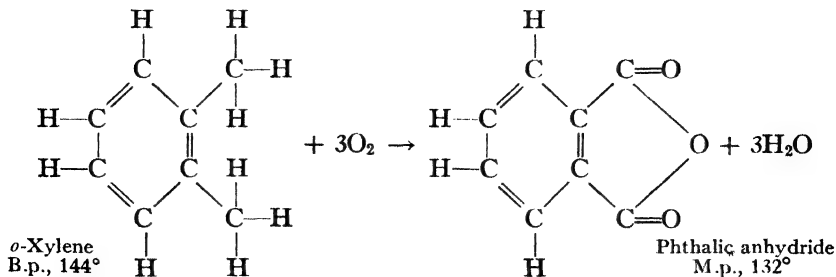




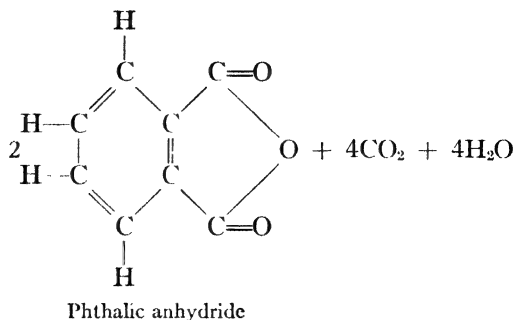
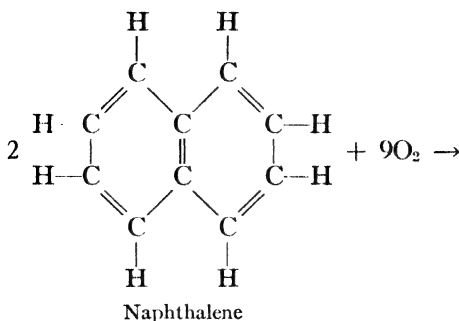
When an aromatic hydrocarbon with a hydrocarbon side-chain is chlorinated, the chlorine will react with the side-chain in the presence of sunlight and in the absence of a metallic catalyst; in the presence of a metallic catalyst, the substitution will take place on the ring.

Sodium benzoate is used very widely as a food preservative ("Not over $\frac{1}{10}$ of 1% benzoate of soda"), and the esters of benzoic acid are used in perfumery.

o-Xylene is oxidized by air in the presence of a catalyst to prepare *phthalic anhydride*.



But the main source of phthalic anhydride is a similar oxidation of *naphthalene*, which may be considered an *ortho* substituted benzene.



The preparation of phthalic anhydride is the only important use of naphthalene other than as a moth repellent (*moth balls*). Phthalic anhydride (Fig. 188) is produced to the extent of about 200,000,000 pounds annually for use in the preparation of plastics (Chapter 32).

EXPLOSIVES

Several compounds (nitroglycerine, glycol dinitrate, **TNT**) have been mentioned that are useful because of their ability to decompose very rapidly with the liberation of a large amount of energy (in the form of heat and light) and gas. The simple ability to explode, however, does not make a compound a useful explosive; many other factors, such as non-explosiveness under conditions of manufacture, transportation, and storage, must be considered. The ease of detonation (explosion) and the rapidity of the reaction govern the use of the explosive. Those which tend to explode more slowly and exert a push rather than a



Figure 188. A truckload of crude phthalic anhydride. (*Courtesy of E. I. duPont de Nemours & Co.*)



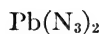
Figure 189. Thousands of tons of rock being loosened by dynamite. (*Courtesy of the Portland Cement Association.*)

shattering blow are used as propellants; the difference in action is somewhat similar to the effect of a sharp blow with a hammer compared with the same energy expended in a slow push. The standard propellant used in the United States is nitrocellulose powders (Chapter 29), while Great Britain, Italy, and Germany use a mixture of nitrocellulose and nitroglycerine (*cordite*).

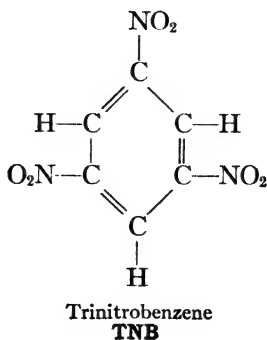
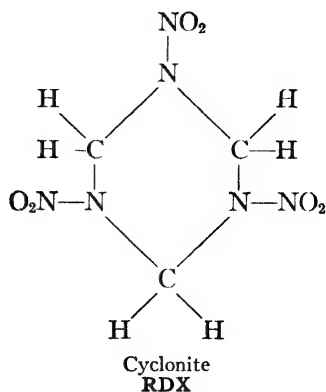
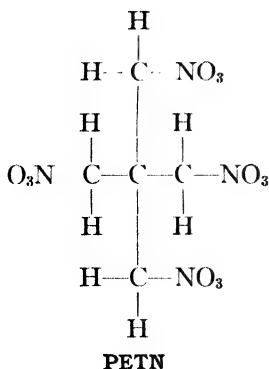
A number of other compounds both inorganic and organic are also used as explosives for special purposes. The formulas of several of the more important ones follow:

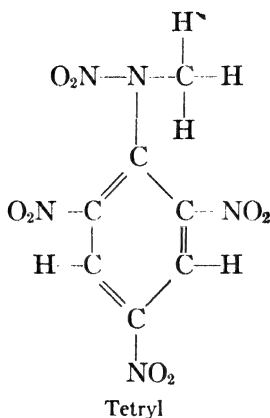
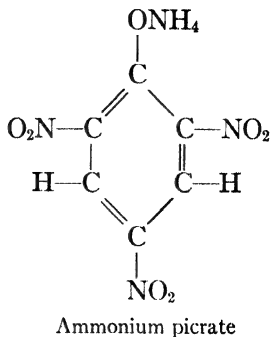
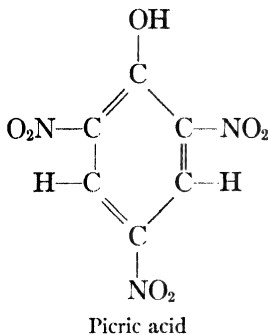


Mercuric fulminate



Lead azide





These non-propellant explosives are classified as to their sensitivity to shock of impact, which is the most important factor in determining their specific application. Most of the high explosives are very difficult to explode by ordinary means; hence a *detonator* such as mercury fulminate or lead azide is used. These compounds explode by percussion, and their explosion sets up vibrations that cause the explosion of the main body of the explosive. Mercury fulminate is used in small percussion caps and electric squibs. Lead azide is preferred for military use because it is slightly less sensitive, thus reducing the possibility of accidental or premature detonation.

Tetryl is intermediate in sensitivity between the detonators and the high explosives and is used as a *booster* explosive. **TNT** is not exploded

by a detonator, but tetryl is; the booster is therefore exploded by a detonator, and the **TNT** is in turn exploded by the booster. Picric acid has the right sensitivity, but it is not used extensively as a booster, for its acid character makes it too corrosive.

TNT is the most widely used high explosive for shells and air-borne demolition bombs, for it can withstand the shock of being fired from

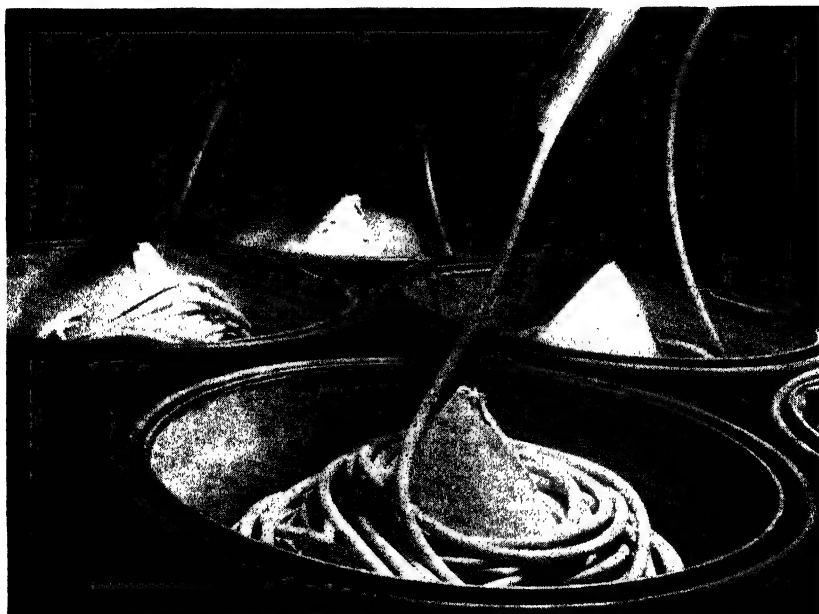


Figure 190. Cords of smokeless powder being collected after pressing into suitable size. (Courtesy of E. I. duPont de Nemours & Co.)

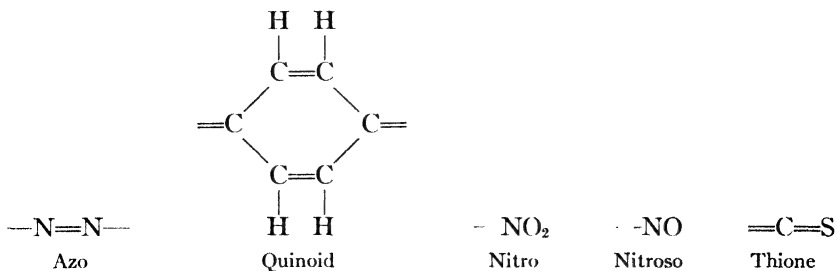
a gun and can be caused to explode by a detonator-booster element. It has the added advantage of melting below 100° and can be poured into shells and bombs. Trinitrobenzene (**TNB**) is a more powerful explosive, but both its high melting point and difficult method of preparation mitigate against its use. Ammonium picrate might also replace **TNT** if it had a melting point sufficiently low to permit easy shell loading.

PETN is a high explosive that is sensitive enough to be detonated by the impact of a rifle bullet. It is used chiefly in the detonating fuse Primacord, a waterproof textile filled with powdered **PETN**. **RDX** (*cyclonite*) is a recently developed high explosive.

DYES

Light is made up of rays of varying wave lengths, those having a wave length between 0.00039 and 0.00076 mm. being visible to the human eye. When the wave lengths are shorter, the light is called ultraviolet; and when they are longer, they are in the infrared region. White light is a mixture of all the visible wave lengths. If any of the wave lengths in the visible range are removed by absorption or are missing for any other reason, the resulting light will be colored.

All molecules have the ability to absorb light waves; but usually this absorption is of wave lengths in the ultraviolet region, and the compounds appear colorless. There are, however, a number of compounds that do have the ability to absorb light waves in the visible range, and the colors of these compounds are dependent upon the wave lengths absorbed. Nearly all colored organic compounds are characterized by having a number of double bonds in their molecules (aromatic compounds) and of containing one or more of the following *chromophore* (Greek *chroma*, color; *phore*, bearer) groups:



A compound is not a dye simply because it is colored. To be a dye a compound not only must be colored but also must have the ability to impart that color to some other material. All colored compounds that can serve as dyes have, in addition to chromophore groups, certain groups that both intensify the color and give the compound the ability to adhere to certain fibers such as silk or wool. The following list includes some of the more important of these *auxochrome* (Greek *auxo*, increase) groups:



The *synthetic-dye industry* had its start in one of those accidents which, in the hands of a competent man, sometimes lead to totally unexpected results. In 1856 William Henry Perkin (Fig. 191) was an assistant in the Royal College of Chemistry. He was only eighteen years old and somewhat inexperienced, and having a little spare time

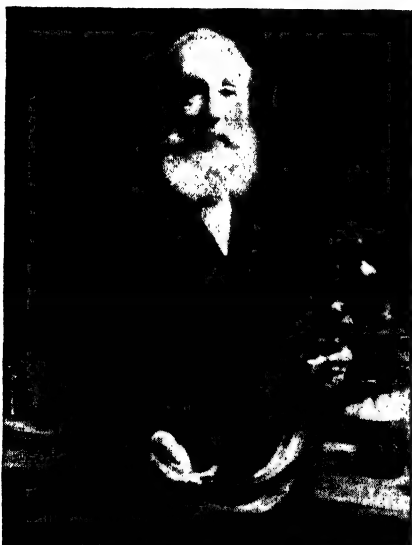


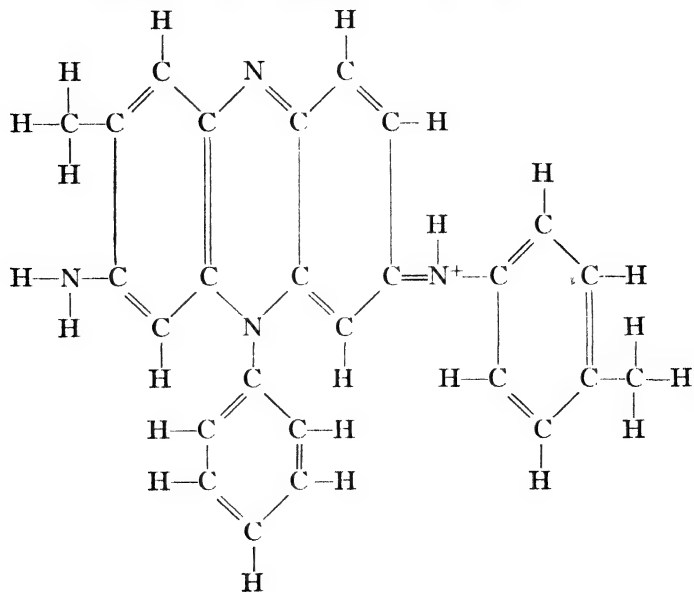
Figure 191. William Henry Perkin. This picture was made many years after he had discovered mauve. (Courtesy of The Edgar Fahs Smith Memorial Collection in the History of Chemistry, The University of Pennsylvania.)

on his hands he decided to synthesize quinine in his laboratory at home. In one of his experiments he took aniline and heated it in the presence of an oxidizing agent; the resulting black precipitate contained about 5 per cent of a purple dye (*mauve*)—the first synthetic dye. A year later Perkin was in the synthetic-dye business, selling mauve at the same price per ounce as platinum. Incidentally, quinine was not synthesized until 88 years later (1944).

The search for dyes from coal compounds resulted in the commercial production of the red dye, fuchsin (rosaniline) in 1859, the azo dye aniline yellow in 1863, and synthetic alizarin in 1871—a great industry had been born.

The remarkably rapid growth of the dye industry can be appreciated better after noting the complex molecules with which the dye chemist had to work. Table 17 gives the formulas of a few compounds representative of some of the different types of dyes. At present over 400 different dyes are manufactured annually with a value of 150,000,000 dollars.

TABLE 17. The Formulas of Several Types of Dyes



Mauve

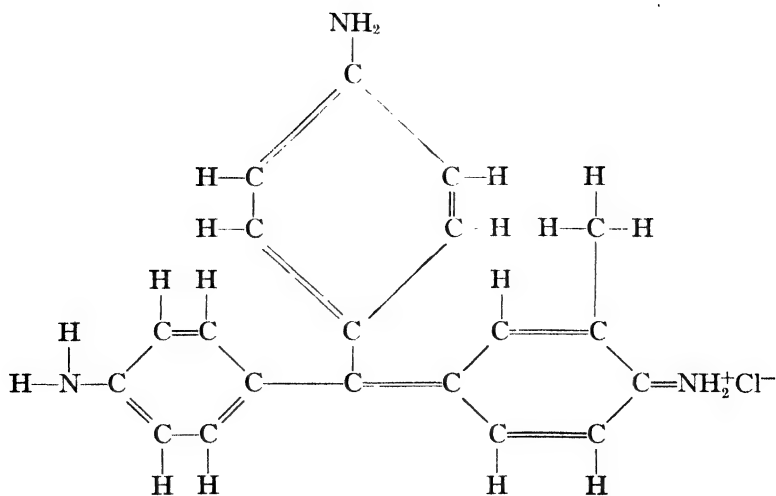
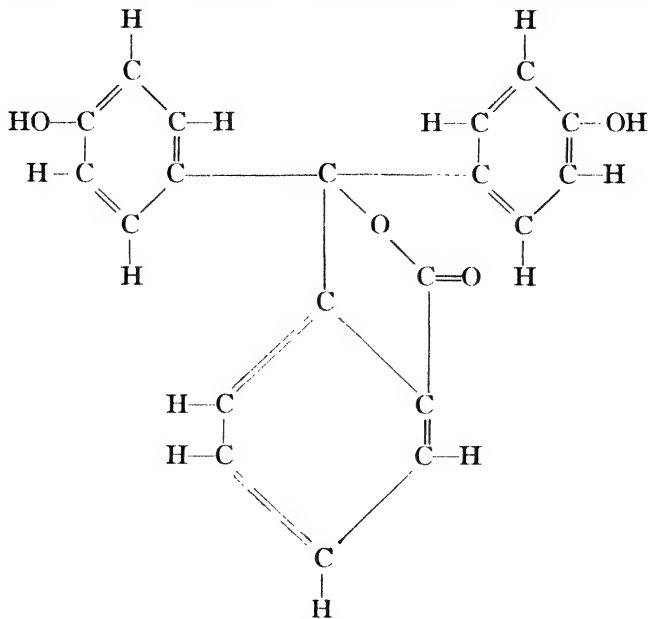
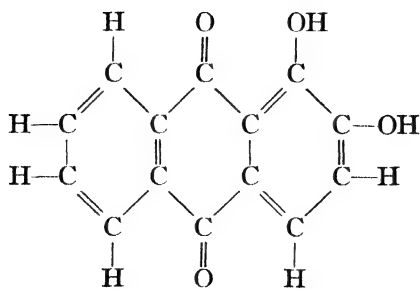
Fuchsin (magenta)
A triphenylmethane dye

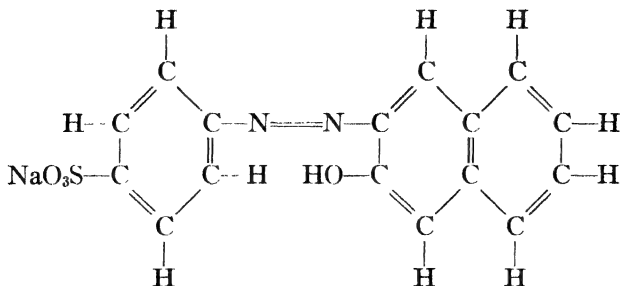
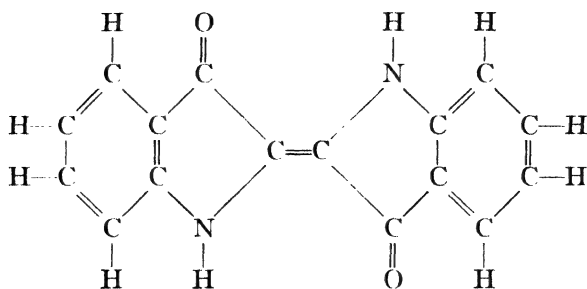
TABLE 17. The Formulas of Several Types of Dyes (*Continued*)

Phenolphthalein
A phthalein dye



Alizarin
An anthraquinone dye

TABLE 17. The Formulas of Several Types of Dyes (Continued)

Orange II
An azo dyeIndigo
An indigoid dye

Dyes are classified with respect both to their structure and to the manner of application.

The simplest method of dyeing is *direct dyeing* by contact of the fiber, usually silk or wool, with a hot solution of the dye. Only a few dyes will dye cotton directly. *Vat dyes* are those where a soluble form of the dye is absorbed by the cloth and then changed to an insoluble form by air oxidation. The dark-blue indigo dye is the best known of the vat dyes.

For those dyes which will not dye cotton, rayon, linen, and similar fibers directly, it is necessary to use a *mordant* (Latin *mordere*, to bite). The usual mordant is aluminum hydroxide or a similar metal hydroxide, which has the ability to hold firmly to both the fiber and the dye. A typical dye requiring a mordant is alizarin. Both alizarin (madder) and indigo were for centuries the leading dyes, both because of their fast colors and because they occur in nature.

In some cases the dyes are made within the fibers that are being

dyed. This is possible by saturating the cloth with one of the two chemicals that will react to form the dye, then transferring the cloth to a solution containing the other compound. The dyes thus produced are formed within the fibers and consequently are very resistant to removal. This procedure is frequently used with azo dyes and is called *ingrain* dyeing.

Indicators. Some dyes have the ability to change color when a solution becomes acid or alkaline and are very useful to indicate whether a solution is acidic or basic; hence the name, indicator (Chapter 15). The naturally occurring dye *litmus* is a common indicator, usually employed in the form of dyed strips of paper (*litmus paper*). Phenolphthalein, which is colorless in acid solutions and pink in basic solutions, is also used as an indicator and as a laxative (*e.g.*, Ex-Lax).

EXERCISES

1. *New terms:* chlorination, *ortho*, *meta*, *para*, phenol, nitration, sulfonation, side-chain, detonation, propellant explosive, detonator, booster explosive, high explosive, chromophore, auxochrome, direct dyeing, vat dyeing, mordant, ingrain dyeing, indicator.
2. What are the two large natural sources of hydrocarbons?
3. Write the formula of the oxidation product of symmetrical trimethylbenzene.
4. What is the chromophore group in each of the dyes listed in Table 17?
5. What is the auxochrome group in each of the dyes listed in Table 17?
6. What is the basic difference between a propellant explosive and a high explosive?
7. Why is benzene considered the most important aromatic hydrocarbon?
8. Write equations for the following indicated reactions of toluene (in each case give only the mono-substitution product): (a) chlorination in the presence of an iron catalyst; (b) nitration; (c) sulfonation; (d) chlorination with no catalyst other than sunlight.
9. What is the difference between vat dyeing and ingrain dyeing?
10. What is the etymology of the words chromophore and auxochrome?
11. Does the structure given for phenolphthalein in Table 17 represent the colored or colorless form?

12. Give two important uses for each of the following compounds: (a) naphthalene; (b) phenol; (c) toluene; (d) benzoic acid; (e) phenolphthalein.
13. Upon what non-chemical industry is the amount of chemicals obtained from coal dependent?
14. In what significant way does **PETN** differ in structure from the other high explosives whose formulas are given in this chapter? What other high explosive does it resemble in structure?
15. Give three uses of cresols. Why would it not be necessary to separate the three isomers for these uses?
16. Are all colored compounds dyes? Explain.
17. Write equations showing the preparation of the following compounds from benzene and any other chemicals needed: (a) **DDT**; (b) phenol; (c) aniline; (d) trinitrobenzene; (e) picric acid.

COLLATERAL READING

BARNETT: "Explosives," D. Van Nostrand Company, Inc., New York, 1919.

DAVIS: "The Chemistry of Powder and Explosives," John Wiley & Sons, Inc., New York, 1943.

FIESER and FIESER: "Organic Chemistry" (abridged), D. C. Heath and Company, Boston, 1944, Chapters 12, 21, and 31.

READ: "Industrial Chemistry," John Wiley & Sons, Inc., New York, 1943.

WILLIAMS and HATCH: "Introduction to Organic Chemistry," D. Van Nostrand Company, Inc., New York, 1948, Chapters 23 and 35.

Biological Chemistry

BIOLOGICAL (or physiological) chemistry, as the name implies, is that branch of chemistry which treats of living organisms and their chemistry. One of the very important phases of biological chemistry pertains to foods and the relation of food to the growth and normal functioning of the body. The chemical nature of fats and their use as both a food and a source of chemicals have been discussed in Chapter 27; in the present chapter we shall explore the role played by the other two major foods, carbohydrates and proteins. In addition there will also be noted the essential part taken by the enzymes, vitamins, and hormones in making it possible for the body to utilize these fats, carbohydrates, and proteins.

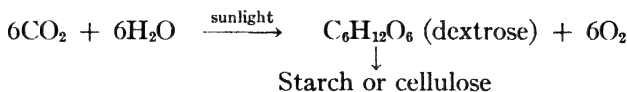
CARBOHYDRATES

The *carbohydrates* (saccharides) are a class of naturally occurring compounds that comprises the sugars, starch, and cellulose (wood, cotton, etc.). They are the most important compounds in plants and animals, where they serve as a source of energy, form the supporting tissues of plants, and are probably the biological precursors of the fats and proteins. Carbohydrates are characterized by having an empirical formula (CH_2O) which suggests that they are hydrates of carbon; hence the name carbo-hydrate. As with so many chemicals and classes of chemicals that occur in nature, the original name was given before the true nature of carbohydrates had been ascertained, a situation similar to the naming of a child before it is born.

Carbohydrates are actually polyhydroxy aldehydes and ketones and are complex compounds. Our chemical knowledge of them, as with the fats, is mainly derived from the study of their hydrolysis products. Fortunately the building units (hydrolysis products) of sugars, starch, and cellulose are relatively simple compounds containing six carbon atoms, five hydroxyl groups, and either an aldehyde or a ketone group.

The problem is further simplified by the fact that starch and cellulose are formed from only one building unit—*dextrose* (*glucose*).

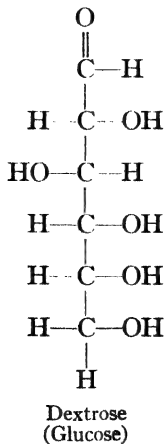
The origin of these six carbon building units in plants is one of the major unsolved problems of chemistry. About all that is known is that plants take in carbon dioxide and water and, through the catalytic activity of the green coloring matter in the plants, *chlorophyll*, and the energy furnished by sunlight, produce carbohydrates and oxygen. A typical equation may be written.



The process is called *photosynthesis* and probably involves at least four separate steps. It is hoped that by the use of radioactive carbon and tracer techniques (Chapter 6) this secret of nature will be revealed. This is of interest here because green plants are the primary source of organic chemicals.

Carbohydrates are classified according to the number of building units in their molecules as either monosaccharides, disaccharides, or polysaccharides.

Monosaccharides. The most important monosaccharide is *dextrose* (glucose, grape sugar), which occurs in grapes and other fruit. There are several structural formulas that can adequately represent dextrose depending upon its particular environment. The following formula is the simplest, and it is adequate for most purposes:



Dextrose is about three-fifths as sweet as ordinary table sugar and is used by the confectionery trade as a sweetening agent. For home consumption it is sold in a concentrated solution as corn sirup (Karo sirup). Dextrose has at times been widely advertised as an energy food, and as frequently happens there is a modicum of truth in the

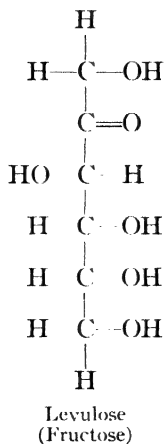


Figure 192. Filling tank car with corn sirup. About 1000 tank cars of corn sirup are shipped each year. (Courtesy of the Corn Products Refining Co.)

claim. Dextrose is the primary energy food of the body and the only carbohydrate that the body can utilize directly. If table sugar or starch is eaten, the body must first exert energy to change it to dextrose; if dextrose is eaten, utilization takes place without this initial loss of energy. It is questionable, however, whether or not a bar of candy will furnish a significant amount of extra energy because of its dextrose content.

The only commercial source of dextrose in the United States is corn-starch, from which over one billion pounds is produced annually. Crude corn sugar is also used in the rayon, brewing, tanning, and fermentation industries.

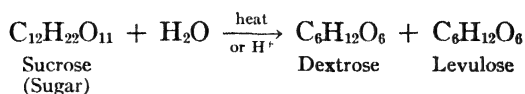
The only other monosaccharide of major importance is *levulose* (fructose, fruit sugar), which occurs to some extent in fruits and is one of the two hydrolysis products of table sugar. It is many times sweeter than table sugar and is responsible for the sweetness of honey. Levulose is obtained commercially from a carbohydrate (*inulin*) from dahlia tubers and the Jerusalem artichoke. It is the only common carbohydrate containing a ketone group.



Levulose cannot be utilized directly by the body, but it is changed into dextrose in the intestines and then assimilated.

Disaccharides. The disaccharides are composed of two monosaccharide units that have joined together with the elimination of a molecule of water. Their molecular formulas are $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, and this formula will be used because the structural formulas are complex and in many cases are still in doubt. The disaccharides are usually characterized by their hydrolysis products.

The only disaccharide produced in large amounts is *sucrose*, or *table sugar* (sugar). Sucrose is characterized by its ready hydrolysis using either acid or heat to give a molecule of dextrose and a molecule of levulose.



Sucrose is widely distributed in nature, but sugar beets and sugar cane are the only two sources from which it is obtained commercially.

Sugar beets furnish about one-sixth of the 80 pounds per capita consumption of sugar and are grown in many of the states. Sugar cane is grown in only a very few of the Gulf Coast states, and the bulk of the cane sugar is imported from Cuba and other semi-tropical countries. *Maple sugar* is a minor source of sucrose; it is used, not for its sucrose content, but for the flavor imparted to it by impurities.

The process of extracting and purifying the sugar from either beets or canes is essentially the same, the major difference being in the manner of separating the sugar from the plant. Thin slices of the beets are placed in water, which dissolves the sugar in the beets; the sugar from sugar cane is obtained by crushing the stalks between rollers, which expresses the juice. In either case the sugar solution contains many impurities which must be removed before pure crystalline sugar is produced. Calcium hydroxide (slaked lime) is added to the solution for the precipitation of the organic acids and proteins present. The solution is then treated with carbon dioxide to remove the excess base and filtered. The sugar solution is concentrated by evaporation, and a crude brown sugar crystallizes. The impure brown sugar is further purified by dissolving it in water and decolorizing with charcoal, followed by recrystallization. This process is repeated several times and results in a product of very high purity—99.8 to 99.9 per cent pure sucrose regardless of whether the sugar came originally from beets or cane.

Molasses, the dark-brown residual solution from which no more crystalline sugar can be obtained, still contains an appreciable amount of sucrose and is used in the production of acetone, butyl alcohol, ethyl alcohol, yeast, citric acid, and vinegar by fermentation, and as a live-stock feed. The sugar cane, after the juice has been expressed, is called *baggasse* and is used for the manufacture of wallboard (Celotex).

Sucrose has the distinction of being the pure organic compound produced in the largest quantity; yet it is not used as a raw material by the chemical industry. This is strange, since the chemical industry almost inevitably utilizes any pure material produced in quantity at a low cost. Extensive research is in progress at present to remedy this situation.

The use of sugar as a sweetening agent and as a food needs no elaboration here. When sugar is heated to about 200°C., it melts and turns brown (caramelizes); *caramel* is used to color many foods and beverages.

The other two important disaccharides are *lactose* and *maltose*. Lactose (milk sugar) is present in both cow's milk (5 per cent) and human milk (7 per cent) and is important because, upon hydrolysis, it yields dextrose and *galactose*, a monosaccharide essential for the normal development of the nervous system. Lactose is obtained commercially from whey and is a by-product of the cheese industry.

Maltose is a hydrolysis product of starch and is present in considerable amounts in corn sirup. It is also formed when barley germinates and is intimately associated with fermentation (*vide infra*). Maltose is composed of two dextrose units.

Polysaccharides. The polysaccharides are composed of many dextrose units and have the general formula $(C_6H_{10}O_5)_n$ where n is a number from about 10 to 20 or more depending upon the particular polysaccharide. The polysaccharides are divided into those which are used as foods and those which are not.

Starch is the most important of the food polysaccharides. It is found in many plants, the principal ones being corn (50% starch), potatoes (20% starch) and rice (75% starch). Starch is prepared commercially from corn by the mechanical process of grinding and washing. It is used in laundry work, cooking, the manufacture of paste, and in the preparation of dextrose and dextrin.

Dextrin is a polysaccharide formed when dry starch is heated to 200 to 250°C.; it is somewhat sweet in taste and is more easily digested than starch. This accounts in some measure for the use of toast as a food for convalescents, for the toasting changes some of the starch of the bread into dextrin. Dextrin has strong adhesive properties and is used on postage stamps, and this may explain an unaccountable gain in weight by stamp lickens.

Starch is the reserve carbohydrate in plants, and *glycogen* is the reserve carbohydrate in animals. Glycogen is synthesized by the body from dextrose and from certain compounds formed during muscular activity as well as from some of the hydrolysis products of proteins. It is composed of 12 to 18 dextrose units and is stored in the liver, where it is available to supply dextrose to the body when energy is needed quickly.

Cellulose is a non-food polysaccharide of great importance. It is composed of dextrose units the same as starch; but, because of a slightly different form of linkage between the dextrose molecules, the body is

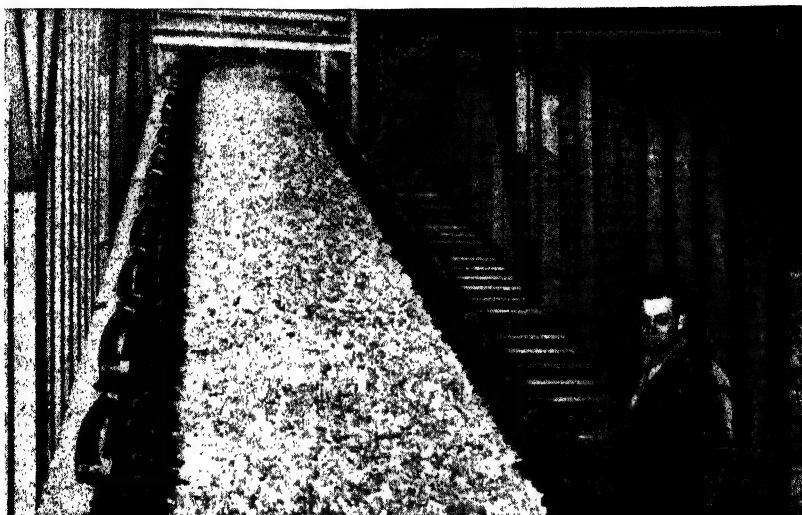


Figure 193. Wood chips being conveyed to a digester in the preparation of pure cellulose from wood. (*Courtesy of the Weyerhaeuser Timber Company.*)



Figure 194. Top of digesters used in the preparation of pure cellulose from wood (*Courtesy of the Weyerhaeuser Timber Company.*)

not able to use cellulose as a food. During World War II, however, German chemists devised a process of acid hydrolysis that promises partly to solve the ever-present problem of an increasing population and a relatively stable food supply (Chapter 31).

Cellulose is the wood-like portion of all plants, although wood itself is not pure cellulose. Wood contains, in addition to cellulose, 20 per cent lignin (a binding material), 20 per cent complicated cellulose-like

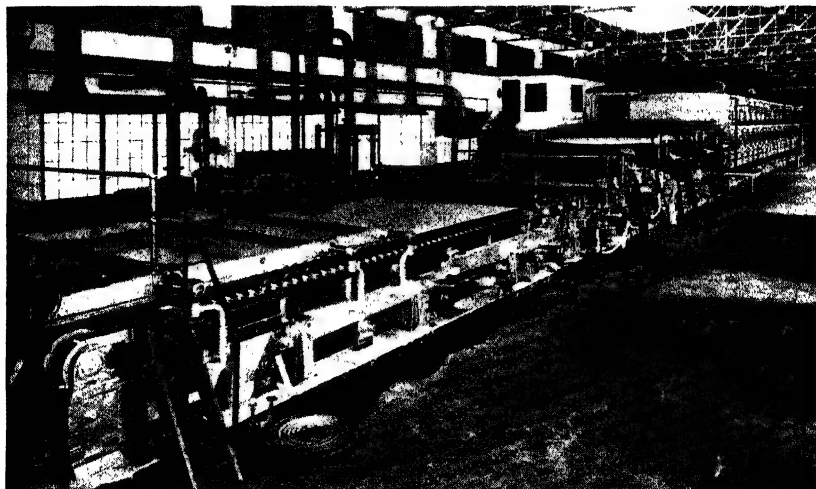


Figure 195. A Fourdrinier machine used for the production of paper. (*Courtesy of the Weyerhaeuser Timber Company.*)

compounds, and 8 per cent mineral salts. Cotton, on the other hand, is essentially 100 per cent cellulose. At present wood and cotton are the two important sources of cellulose.

Most of the cellulose produced in this country is used in the manufacture of *paper*. In general the wood is cut into small pieces and treated with calcium bisulfite or some other chemical (NaOH) to remove the lignin; then, after bleaching, various materials are added, and the mixture is then layed to make sheets of paper. The type of paper determines the nature of the material added: if a porous water-absorbing paper or pure wood pulp is desired, nothing will be added; if a heavy, slick paper is to be made, there will be added materials such as clay and barium sulfate. A block of wood 2 inches high, 3 inches wide, and 4 inches long is required to supply the pulp in a 24-page newspaper. High-grade paper is made from rags, preferably linen rags.

Cellulose contains several hydroxyl groups in each of its dextrose units and consequently is amenable to chemical reactions typical of alcohols. One of the most important of these reactions is that of nitra-

TABLE 18. Some Common Carbohydrates
(*Saccharides*)

<i>Class</i>	<i>Name</i>	<i>Other names</i>	<i>Source</i>	<i>Building units</i>
Monosaccharides . . .	Dextrose	Glucose, grape sugar	Hydrolysis of starch, fruits	
	Levulose	Fructose, fruit sugar	Hydrolysis of inulin	
	Galactose	Hydrolysis of lactose	
Disaccharides.....	Sucrose	Table sugar, sugar	Sugar cane, sugar beets	Dextrose, levulose
	Lactose	Milk sugar	Milk	Dextrose, galactose
	Maltose	Malt sugar	Hydrolysis of starch, malt	Dextrose, dextrose
Polysaccharides. . .	Starch	Corn, rice, potatoes, etc.	Dextrose
	Cellulose	Wood, cotton	Dextrose
	Glycogen	Animal starch	Livers	Dextrose
	Dextrin	Starch	Dextrose
	Inulin	Jerusalem artichoke	Levulose

tion to form *cellulose nitrate*. The reaction is carried out in a manner similar to that used in the production of nitroglycerine (Chapter 26).

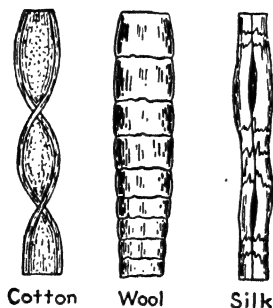


Figure 196. The appearance of natural fibers as viewed under a microscope.

The extent of the reaction and the use of the product is determined by the nitrogen content of the cellulose nitrate. If the product contains about 13.5 per cent nitrogen, it is the explosive *guncotton* and it is

used in smokeless powder, gelatin dynamite, cordite, etc. The product that is not so extensively nitrated (10 per cent nitrogen) is called *pyroxylin* and is used to make lacquers, artificial leather, celluloid, and collodion. Nail polishes contain pyroxylin dissolved in various solvents mentioned in Chapter 27.



Figure 197. Sheets of cellulose being added to steeping press, where the cellulose is converted to sodium cellulose. (Courtesy of E. I. duPont de Nemours & Co.)

Fibers. Historically the fibers for the manufacture of fabrics were linen, cotton, silk, and wool (Fig. 196). The first two are from plants and are composed of cellulose; the second two are of animal origin and are protein in nature. Because of the low cost of cotton, a large amount of time and effort have gone into methods of improving cotton fiber or changing cellulose into a new and better fiber. The fruit of these labors is *rayon*.

About 95 per cent of the 600 million pounds of rayon produced annually is made by the viscose and acetate process. In the *viscose process* pure cellulose from either wood or cotton linters is treated with

sodium hydroxide to form sodium cellulose (Fig. 197), and the sodium cellulose is aged several days. The sodium cellulose is then caused to react with carbon disulfide, and cellulose xanthate is formed. The xanthate is dissolved in sodium hydroxide solution to form a thick viscose liquid. This liquid is forced through tiny holes in a spinneret into an acid bath, where the xanthate is decomposed and cellulose is

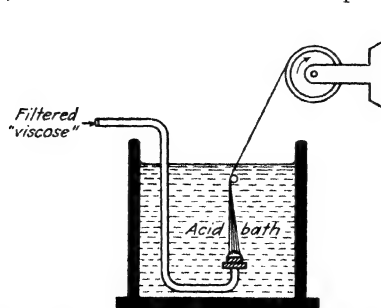


Figure 198. Spinning of viscose rayon yarn.

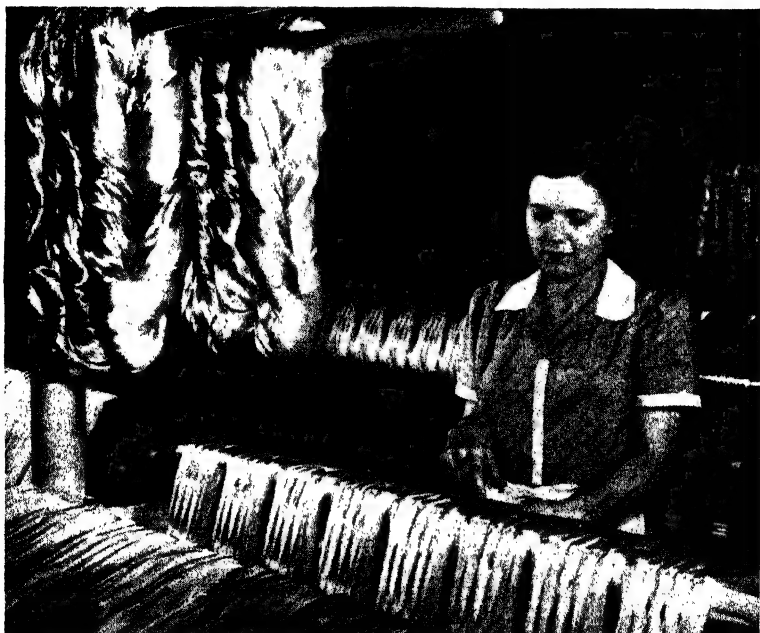


Figure 199. Skeins of viscose process rayon yarn. (Courtesy of E. I. duPont de Nemours & Co.)

regenerated in the form of fibers (Fig. 198). *Cellophane* is made in the same way except that the regenerated cellulose is run through rollers to produce a thin sheet. To make 1 ton of rayon there are required 2 tons of sodium hydroxide, $\frac{1}{2}$ ton of carbon disulfide, $1\frac{1}{2}$ tons of sulfuric acid, and $1\frac{1}{10}$ tons of cellulose.

In the *acetate process* the cellulose is treated with acetic anhydride

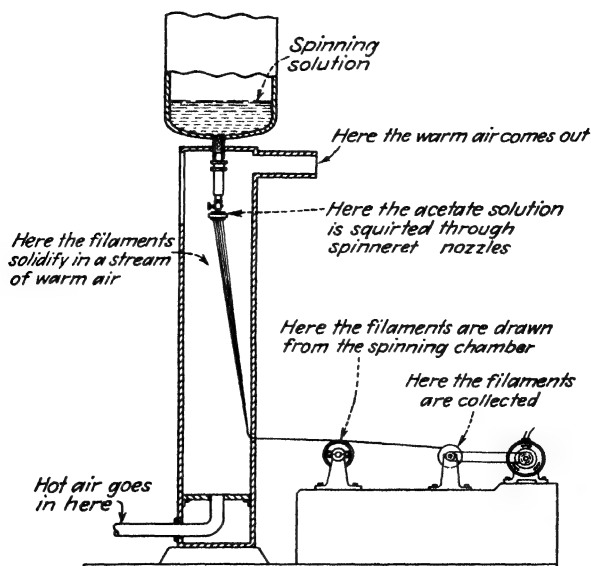


Figure 200. Spinning of cellulose acetate (Celanese) yarn. (Courtesy of the Celanese Corporation of America.)

in acetic acid to form cellulose acetate. The cellulose acetate is obtained as a precipitate by adding the mixture to water. The acetate is then dissolved in acetone and forced through spinnerets into warm, humid air (Fig. 200), and filaments of *acetate rayon* (Celanese) are produced by the evaporation of acetone. Acetate rayon is a compound of cellulose and not a regenerated cellulose; hence it is soluble in nail polish and nail-polish remover.

Within recent years there have been developed a number of new fibers, although nylon is undoubtedly the best known because of its use in hosiery, brushes, fishing leaders, tennis-racket strings, surgical sutures, etc. With the exception of the regenerated protein fibers and fiber glass, all of these fibers are closely related to synthetic rubber in that they are formed from simple building units. Small molecules are

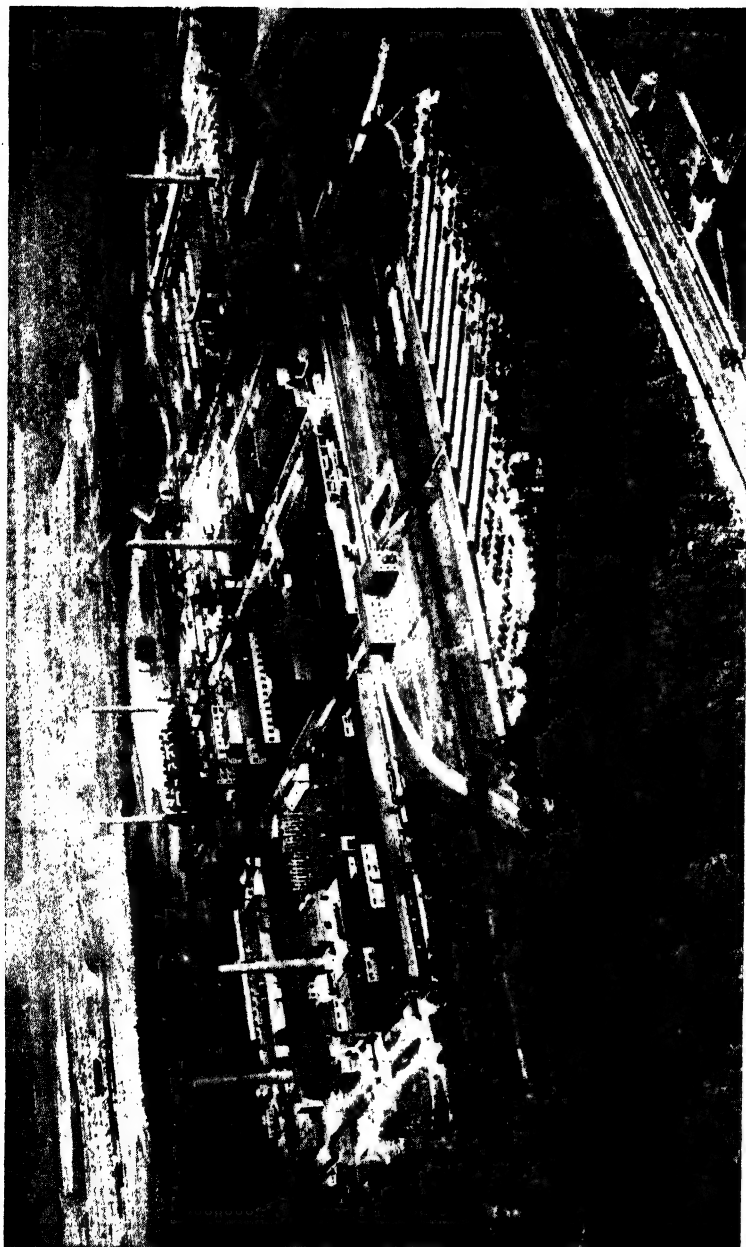


Figure 201. Aerial view of rayon and cellophane plants near Richmond, Va. (Courtesy of E. I. duPont de Nemours & Co.)



Figure 202. Nylon, made from coal, air, and water, being fed into spinning machine where it is melted and extruded into fibers. (*Courtesy of E. I. duPont de Nemours & Co.*)

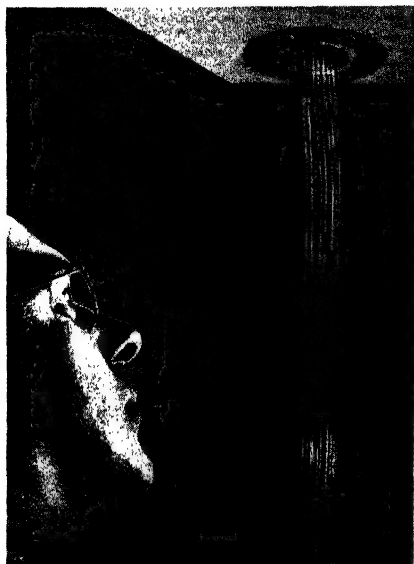


Figure 203. Nylon being extruded from spinneret of spinning machine. These filaments are wound together to make nylon yarn. (*Courtesy of E. I. duPont de Nemours & Co.*)

caused to react with themselves (polymerize) or a co-present molecule of similar type to form high-molecular-weight long-chain molecules which are suitable for spinning in a manner similar to that used for cellulose acetate. Fibers of this type usually have more elasticity than cotton but appreciably less than rubber. Table 19 lists a few of the more important synthetic fibers.

TABLE 19. Synthetic Fibers

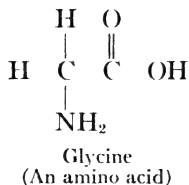
<i>Name</i>	<i>Building units</i>	<i>Formula of building units</i>
Rayon	(Regenerated cellulose)	
Bemberg rayon	(Regenerated cellulose)	
Celanese	(Cellulose acetate)	
Nylon (1935)	Hexamethylenediamine	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{H}_2\text{N}-\text{C}-(-\text{C}-)_4-\text{C}-\text{NH}_2 \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$
	Adipic acid	$\begin{array}{c} \text{O} \quad \text{H} \quad \text{O} \\ \quad \quad \\ \text{HO}-\text{C}-(-\text{C}-)_4-\text{C}-\text{OH} \\ \\ \text{H} \end{array}$
Soybean fiber (1937)	(Regenerated soybean protein)	
Vinyon (1938)	Vinyl chloride	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{Cl} \end{array}$
	Vinyl acetate	$\begin{array}{c} \text{H} \quad \text{O} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{O}-\text{C}=\text{C}-\text{H} \\ \\ \text{H} \end{array}$
Saran (1940)	Vinyl chloride	
	Vinylidene chloride	$\begin{array}{c} \text{H} \quad \text{Cl} \\ \quad \\ \text{H}-\text{C}=\text{C}-\text{Cl} \end{array}$
Aralac (1940)	(Regenerated milk protein)	
Velon	Vinylidene chloride	
	Unspecified copolymer	
Vinyon N (1947)	Vinyl chloride	
	Acrylonitrile	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}=\text{C}-\text{C}\equiv\text{N} \end{array}$
Fiber glass	Glass	

PROTEINS

The last of the basic foodstuffs to be discussed is by far the most complicated and the most important. We could live for a long time on a diet deficient in fats and carbohydrates, but we must have a minimum of proteins (Greek *proteios*, primary) in our daily diet to replace muscle tissue destroyed in the course of normal bodily activity.

Proteins may be described as complex nitrogenous compounds that on hydrolysis yield amino acids. Once again we find a class of compounds so complex that they must be characterized in terms of their simpler hydrolysis products. The proteins are even more complex than the simple definition would indicate, for frequently they yield on hydrolysis other types of compounds as well as many different amino acids.

An *amino acid* is an organic acid distinguished by having a hydrogen atom on the carbon atom next to the carboxyl group replaced by an amino group (---NH_2). The simplest amino acid is *glycine*.



Of the approximately 25 amino acids so far isolated and identified from different proteins there are 10 that are essential in the human diet. Fortunately these amino acids are present in nearly all of the common proteins. A diet of corn pone and grits, however, is not adequate.

Proteins are widely distributed in plants and animals and serve as structural materials for animals much as cellulose does for plants. The skin, hair, and muscle tissue and the horny material of nails, horns, and hoofs are primarily protein in nature. The plant proteins can in general replace animal proteins in the diet. In the last analysis, man and other higher animals depend wholly upon plants for proteins.

Proteins are difficult to classify because of their complexity. The following classification is the simplest and will serve.

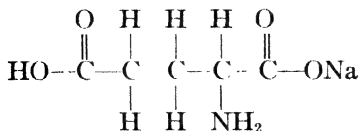
1. *Simple proteins*. Those proteins which yield only amino acids on hydrolysis. Several examples are egg albumin, glutenin of wheat, gliadin of wheat, zein of corn, and keratin found in hair and horn.

2. *Conjugated proteins.* Proteins that contain in addition to amino acids some other molecules such as carbohydrates or phosphoric acid. Casein from milk and hemoglobin from blood are examples.

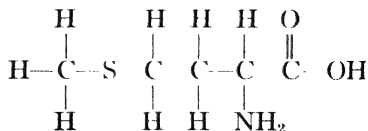
3. *Derived proteins.* These proteins are derived from more complex proteins by hydrolysis.

Proteins furnish a large segment of our population with their livelihood. All of the following industries are primarily concerned with raising or processing proteins: meat raising, meat packing, tanning, fisheries, glue manufacture, cheese making, casein processing, wool and silk textiles, etc.

Several amino acids are produced commercially. *Glutamic acid*, an amino acid, has been shown to increase the intelligence of backward children and also to effect basic personality changes. *Monosodium glutamate* has been used for some years to enhance the flavor of many high-quality prepared foods. It has such strong meat-like flavoring powers that 1 part of it dissolved in 3000 parts of water is still definitely perceptible to the taste. *Methionine* is used in the treatment of starvation and in medicine.



Monosodium glutamate
MSG



Methionine

The annual per capita consumption of meat is 155 pounds, while the protein requirement of a 150-pound person is approximately $\frac{1}{4}$ pound per day.

BIOCHEMICAL CATALYSTS

By this time it should have become apparent that in organic chemistry the use of a catalyst is frequently necessary to increase the rate of a reaction so that a product can be made in a reasonable time. Sometimes catalysts are used to increase the rate of an obscure reaction until it becomes the dominant reaction and thus changes the nature of the products formed. Catalysts play the same role in biochemical reactions.

Enzymes. Biochemical reactions take place at an appreciable rate

only in the presence of specific catalysts called *enzymes*. Enzymes are protein in nature, and one of their more important functions is to catalyze the hydrolysis of fats, carbohydrates, and proteins to their building units, which can be utilized by the body. For example, the tenderizing effect of aging meat is the result of enzymatic hydrolysis of the tough connective tissue. The same result can now be obtained in 30 minutes by using an enzyme (Tendra) obtained from the tropical fruit *Carica papaya*. A number of other pure crystalline enzymes are also available. Enzymes are frequently named to indicate their specific function: *maltase* hydrolyzes maltose, *lipase* hydrolyzes fats, *sucrase* hydrolyzes sucrose, etc.

A large chemical industry has been developed around the fermentation of carbohydrates, which in turn is dependent upon the action of enzymes.

Alcoholic Fermentation. The fermentation of molasses to produce *industrial alcohol* is brought about by the use of yeast, which contains the appropriate enzymes both to hydrolyze the sucrose and to change the monosaccharides into ethyl alcohol and carbon dioxide. The molasses is diluted to a sugar concentration of about 10 to 18 per cent, and the solution is made slightly acid and seeded with yeast. The fermentation proceeds with the evolution of carbon dioxide at 21 to 27°C. for thirty to sixty hours. The alcohol is obtained from the mixture by distillation.

For the preparation of *alcoholic beverages*, starch is the carbohydrate used except when fruit juices are fermented. Yeast does not contain an enzyme with the ability to hydrolyze starch, and it is thus necessary to accomplish this hydrolysis by the addition of *malt*, which contains the enzyme *diastase* that can hydrolyze starch. Malt is barley that has been allowed to sprout for about three days and then dried.

Alcoholic beverages can be divided rather arbitrarily into those which are distilled and those which are not. In the latter class are the beers and wines; in the former class are the brandies, liqueurs, whiskies, rum, gin, etc., which are frequently referred to as "hard" liquors because of their relatively high alcoholic content.

The history of *beer* dates back to at least 1300 B.C., but it was not until about the sixteenth century that a clear distinction was made between beer and ale. *Ale* differs from beer in that no hops are used in the brewing operation, as they are with beer. Both were brewed in

this country as early as the seventeenth century, and beer is today the most widely consumed alcoholic beverage. Beer is made by adding water, hops, and yeast to the mash (malt plus the grain to be used) and allowing the mixture to ferment. After fermentation, the beer is filtered, aged, and bottled. *Bock* beer is a little stronger and has been aged a little longer than ordinary (*lager*) beer.



Figure 204. Adding hops to the brew kettle. (Courtesy of the Gulf Brewing Co.)

Wines are produced by the fermentation of various fruit juices, usually grapes. There are as many wines as there are fruits, but in every instance the process of preparation is the simple one of adding yeast and letting nature do the rest. The fermentation is usually carried out to an alcoholic content of 16 to 17 per cent; then the enzymes are inactivated by heat (*pasteurization*), and the wine is diluted with water to the retail concentration of 6 to 12 per cent. The color and flavor of the wine are dependent upon the fruit used.

Champagne is produced by bottling the wine while fermentation is still actively in progress. This produces a wine that is carbonated by the carbon dioxide produced during fermentation. *Sparkling wines* may

also be made by simply carbonating a wine in a manner similar to that used for making soda water. *Port* and *sherry* are fortified wines. Port comes from Portugal, and sherry has had licorice added to give it its characteristic flavor; their alcoholic content is about 20 per cent. *Vermouth* is a wine that has been fortified with brandy and aromatized with herbs.



Figure 205. View down main aisle in brewery cellar. On the left are carbon dioxide storage tanks. (Courtesy of the Gulf Brewing Co.)

The first distilled liquor ever to be made was brandy made by the distillation of wine. It has long been used for medical purposes, and in the Middle Ages it was considered a panacea for almost every human ill. The most famous brandy is *cognac*, which comes from the district of Cognac in the south of France. Brandies vary in strength but usually contain about 35 per cent alcohol. The quality of brandy increases with age for 20 to 60 years, but beyond that time it begins to "break down."

Liqueurs, developed in the Middle Ages by alchemists and in various monasteries (Benedictine, 1510), are heavy-bodied beverages that have

been strongly flavored, aromatized, and sweetened. Their alcoholic content usually varies between 30 and 45 per cent.

Whisky is the distilled product of the fermentation of grain. There are four true whiskies: Scotch, Irish, Bourbon, and rye. *Scotch whisky* is made by the fermentation of barley in a manner similar to the production of beer but without the hops. The distilled product gets its

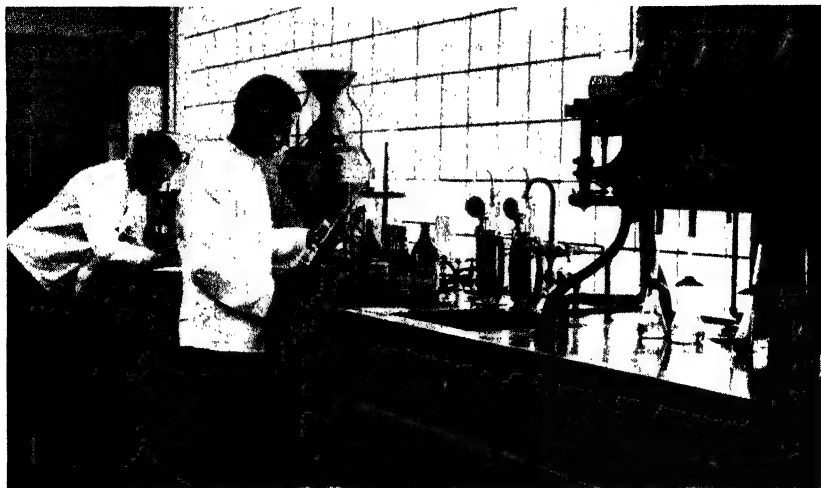


Figure 206. Section view of the control laboratory of a modern brewery. (Courtesy of the Gulf Brewing Co.)

characteristic smoky flavor from peat smoke. Scotch whisky is a blend of straight whisky and grain neutral spirits and is aged at least 4 years in oak casks; it is usually sold at 86.6 proof. The *proof* figure on a whisky is always twice the actual alcoholic content in per cent by volume. *Grain neutral spirits* is the alcohol distilled from an unmalted mash.

Irish whisky is similar to Scotch but without the peat-smoke treatment.

Rye whisky is a typical American product made from a mash containing at least 51 per cent rye, 10 to 40 per cent corn, and about 10 per cent barley malt. *Bourbon* whisky was first brewed by Elijah Craig at Georgetown, Ky., in 1789 and received its name from Bourbon County. It is made from a mash containing at least 51 per cent corn, with the average about 60 per cent corn and the rest rye and

barley malt. Whiskies are aged in charred oak kegs to give them color and stored in heated warehouses.

Bottled in bond whiskies are those which are guaranteed by the government to be at least 100 proof and to have been aged at least 4 years. *Straight* whiskies are distilled from the fermented mash, have no grain neutral spirits added, and are usually 90 to 93 proof. *Blended* whiskies contain less than 50 per cent straight whisky, the rest being grain neutral spirits. They are usually less than 90 proof.

Gin was developed by a Dutch scientist over 300 years ago. It is produced by distilling pure grain spirits and permitting the vapors to pass through a "berry-head" containing juniper and other berries, roots, and aromatic herbs. The vapors retain some of the flavors of the contents of the berry-head.

Rum is distilled from the fermentation products of molasses. It constituted one side of the famous three-cornered trade that made New England prosperous. New England ships took rum to Africa, where it was exchanged for slaves; the slaves were taken to the West Indies and were exchanged for molasses; the molasses was brought to New England to be made into more rum. Rum now comes mostly from the West Indies.

Each country has its favorite alcoholic beverage. Russians prefer *vodka*, which is made from potatoes; the Japanese have their *sake*, from rice; and the Mexicans make *tequila* from cacti. The Germans drink the so-called "beverage of moderation," beer, while in France and the Mediterranean countries wine is preferred. In England one of the most popular drinks is gin, and in the United States whisky is favored by many.

The fermentation reaction is not the simple one pictured by an equation showing ethyl alcohol and carbon dioxide as the only products. Other alcohols (fusel oil) and some acids are also produced; and by changing conditions and enzyme sources the following compounds are made commercially: acetone, butyl alcohol, citric acid, acetic acid, lactic acid, and glycerine.

The making of breads is also dependent upon fermentation. Sugar and yeast are added to the bread dough; the yeast causes the sugar to undergo alcoholic fermentation with the formation of carbon dioxide and alcohol. It is this carbon dioxide which causes the dough to rise. The alcohol is lost during the baking process.

Vitamins and Hormones. Vitamins and hormones are organic compounds that occur in the body in small amounts and have special functions that appear, superficially at least, to be catalytic in nature. The fundamental distinction between vitamins and hormones is that *hormones* are synthesized by the body, whereas *vitamins* cannot be synthesized by the body but must be furnished in the food. The terms "vitamin" and "hormone" are based upon physiological concepts and do not necessarily refer to specific substances. There are a number of compounds with vitamin D activity; thus no specific compound can rightly be called "vitamin D." On the other hand, there is only one vitamin C (ascorbic acid). Vitamins are in general relatively simple compounds, while hormones may be simple or may have the complexity of proteins. Neither the vitamins nor the hormones have chemical characteristics in common.

There are two types of vitamins: (1) those which function only in highly specialized organisms; (2) those which are universal constituents of all living matter and make up part of the catalytic system of all living cells. The "B vitamins" are of the latter type, while all the rest belong to the former class. Table 20 gives the molecular formula, occurrence, and deficiency symptoms of the vitamins. Most vitamins are so widely distributed in nature that any well-balanced diet will supply one with his vitamin requirements. This must be so or all those who lived before synthetic vitamins became available lived something less than a full life.

Hormones are very diverse in nature and function. The simplest compound with hormone-like activity is carbon dioxide, which regulates respiration. The complex sex hormones are classified as either male or female sex hormones, but the classification is not rigorous, for they are not restricted to the sex indicated. These hormones are frequently used in medicine.

Within recent years the use of plant hormones has increased enormously. The use of these hormones will be discussed in the chapter pertaining to agriculture, for it is in agriculture that they are used.

TABLE 20. Vitamins

<i>Name</i>	<i>Molecular formula</i>	<i>Prominent occurrence</i>	<i>Symptoms of deficiency</i>
Vitamin A	Several related compounds exhibit vitamin A activity	Fish-liver oils, egg yolk, butter fat, green and yellow vegetables	Night blindness, temporary sterility in male rats, certain types of infection of epithelial tissue
Vitamin C (ascorbic acid)	$C_6H_8O_6$	Citrus fruits, tomatoes, leafy green vegetables, potatoes	Symptoms of scurvy, <i>i.e.</i> , hemorrhages of skin and gums, palpitation of heart, dental caries, etc.
Vitamin D	More than one compound known to possess vitamin D activity	Milk, fish-liver oils, egg yolks, cereals irradiated with ultraviolet light	The disease known as rickets
Vitamin E	Numerous compounds α Tocopherol ($C_{29}H_{50}O_2$) is the most potent	Wheat-germ oil, cottonseed oil, green leafy vegetables	Permanent sterility, muscular lesions
Vitamin K	Numerous related compounds	Putrefied fish meal, hog-liver fat, alfalfa	Nutritional significance unknown. Useful in treatment of obstructive jaundice, hemorrhages, etc.

"B Vitamins"

Vitamin B ₁ (thiamin)	$C_{12}H_{18}Cl_2ON_4S$	Milk, green vegetables, rice polishings, yeast, fruits, peanuts	Lack of appetite, retarded growth, beriberi, polyneuritis, low gastric acidity, constipation
Riboflavin	$C_{17}H_{20}O_6N_4$	Beef liver (meats in general), eggs, milk	Lack of growth in young, lesions of the lips, etc., in humans
Nicotinic acid	$C_6H_5O_2N$	Meats, whole wheat, rolled oats, green peas	Symptoms characteristic of pellagra
Pyridoxine (B ₆)	$C_8H_{11}O_3N$	Widespread	Dermatitis in rats

TABLE 20. Vitamins (*Continued*)

<i>Name</i>	<i>Molecular formula</i>	<i>Prominent occurrence</i>	<i>Symptoms of deficiency</i>
Pantothenic acid	$C_9H_{17}O_6N$	Milk, eggs, beef liver, cereals, potatoes, etc.	Dermatitis and failure of growth in young animals; gray hair in animals
Biotin	$C_{10}H_{16}O_3N_2S$	Widespread. Produced by numerous kinds of bacteria	
Inositol . . .	$C_6H_{12}O_6$	Occurs generally in animal tissues	Not well known
<i>p</i> -Aminobenzoic acid	$C_7H_7O_2N$	Widespread	

EXERCISES

1. *New terms:* photosyntheses, disaccharides, caramelize, acetate process, amino acid, conjugated protein, enzyme, malt, vitamin, carbohydrate, monosaccharide, polysaccharide, viscose process, protein, simple protein, derived protein, grain neutral spirits, hormone, sized, weighted.
2. Why is the crust of bread somewhat sweeter than the rest of the loaf?
3. What is the basic difference between (*a*) rayon and nylon; (*b*) viscose rayon and acetate rayon?
4. What is the difference between vitamins and hormones?
5. What is meant by 86 *proof* on a bottle of whisky?
6. Name and give the formulas for six different compounds that are produced by fermentation.
7. Write the structural formulas for dextrose and levulose.
8. In what way are the "B vitamins" different from the other vitamins?
9. Why is it necessary to malt corn but not molasses before fermentation with yeast?
10. Classify proteins.
11. List the hydrolysis product or products of each of the following carbohydrates: sucrose, maltose, lactose, starch, cellulose.

12. Is it possible to utilize cellulose as a food? Explain.
13. Is it necessary to supplement a normal well-balanced diet with synthetic vitamins? Explain.
14. If the answer to exercise 13 was no, why are synthetic vitamins made?
15. What, if any, is the difference between cane sugar and beet sugar other than their origin?
16. List four industries that are dependent upon proteins for their raw material.
17. What pure organic compound is produced in the largest amounts?
18. Slaked lime, Ca(OH)_2 , is used in the purification of sugar juice. Write equations illustrating the reactions involved in removing the excess slaked lime.
19. Calculate the total amount of sugar (sucrose) used in this country each year. Assume a population of 145,000,000.
20. If the protein requirement of a 150-pound person is one-fourth of a pound per day, what would this amount to in a year? How does this figure compare with the average consumption of meat in this country?

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Medicinals and Pharmaceuticals

AS STATED in Chapter 20, the history of mankind is replete with accounts of his pursuit of a longer life; man will stop short of nothing in his endeavor to maintain or regain his health. During the Middle Ages the alchemists tried to produce a universal panacea and a means of indefinitely preserving life, but their efforts, of course, met with no success. The concoctions of the alchemists, however, were no worse than some that are sold today, in spite of the vigilance of the Food and Drug Administration. Real progress has come only since the chemist, pharmacist, and medical doctors have joined forces in research. That the results have been spectacular is indicated by the fact that in 1948 the general life expectancy in the United States was 67 years, an increase of a year over 1945 and two years over 1940.

The relationship between the pharmacist and the doctor is evident; the close relationship between the chemist and medicine is not so well known. It is more apparent when one considers that all medicine, even sugar-coated pills, are chemicals, either synthesized or from natural sources. It has been only recently, however, that the chemist has systematically concentrated on the production of chemicals to be used as medicines. Some of the more noteworthy results are the sulfa drugs, antimalarials, penicillin, and the synthetic vitamins and hormones. It is the ultimate goal of the chemist to produce a chemical that will be a specific cure for each disease. This treatment of disease by chemicals is called *chemotherapy*. The earliest and one of the best known examples of chemotherapy was the treatment of syphilis with salvarsan (606) by Ehrlich in 1911.

The relationship between the pharmacist and the chemist is not so close as it was before the advent of packaged drugs. In earlier times not only did the pharmacist compound the medicine, but he also was the chemist who made the chemicals. Even today a pharmacy is called

a chemist's shop in several foreign countries, and some of the early chemical discoveries were made by pharmacists in their spare time. One of the most noted was Karl W. Scheele, who discovered chlorine and glycerine and is considered to be a co-discoverer of oxygen.

The discussion of various medicinals and pharmaceuticals will be under the following rather arbitrary headings: anesthetics, sympathomimetics, analgesics and antipyretics, sedatives, antiseptics, antibiotics, and miscellaneous compounds. Most of the names of the compounds used for medical purposes bear little or no relationship to their structure but are employed because the chemical names are usually too unwieldy. Only a relatively few of the many compounds used in medicine will be mentioned, and these will be those commonly used, especially in proprietary medicines.

A word of caution: This is not a "doctor book," and under no circumstances

should any of the chemicals mentioned be used without the prescription of a physician. "If the headache persists, see your doctor."

Anesthetics. Anesthetics are compounds that have the ability to cause a person to become insensible. *Ether* was the first anesthetic used, and it continues to be the safest and most widely used general anesthetic. Its first use was by Dr. Long (Fig. 207) in Georgia in 1842, but his results were not published. In 1846 Morton, a Boston dentist, successfully demonstrated the use of ether in surgical practice at the Massachusetts General Hospital. At this time the term *anesthesia* (Greek *anaesthesia*, insensibility) was suggested by Oliver Wendell Holmes, who, incidentally, spent as much time crusading against the uncleanness of doctors as he did in being a doctor, professor, poet laureate of Boston, and Autocrat of the Breakfast Table. The question of credit for the discovery of ether as an anesthetic is similar to that of the discovery of oxygen (Chapter 11). A discovery that is not made available by publication is of little practical use.

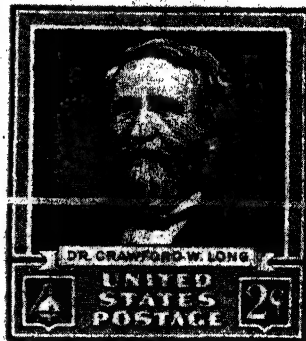
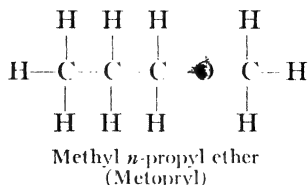
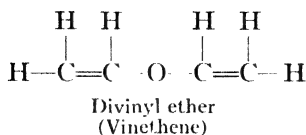
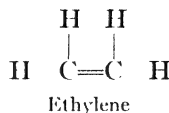
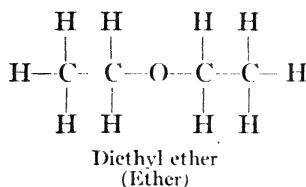


Figure 207. Dr. Crawford W. Long, who first used ether as an anesthetic.

Several compounds have been used in place of ether, but none is as widely used. *Ethylene* (1923)¹ causes a rapid and pleasant induction of unconsciousness with prompt recovery, but it forms explosive mixtures with air, which militates against its use. *Divinyl ether*, Vinethene (1930), is so constituted that it entails the structural features of both ethylene and ether and is about seven times more potent than ether and more rapid in its action. There is some danger in the use of Vinethene, for too deep a plane of anesthesia may be reached. A recent anesthetic of the ether type is *methyl n-propyl ether*, Metopryl (1946), which is said to be more powerful and less irritating and has less disagreeable after-effects than ethyl ether.



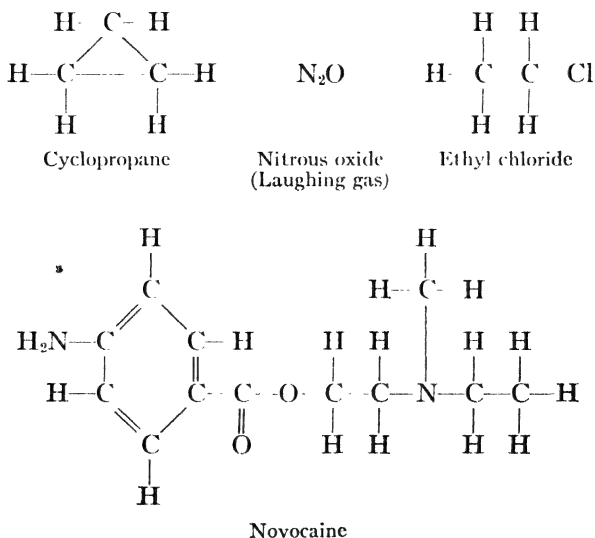
Some compounds with quite different structures have also been used as anesthetics. *Cyclopropane* (1934) is the most potent of the anesthetic gases, and its use does not cause later discomfort as does ether. It is explosive, expensive, and flammable, all characteristics that are undesirable in an anesthetic. In the hands of an experienced anesthetist with special equipment it is safe.

The first compound suggested for use in surgical operations was *nitrous oxide*, laughing gas (1799), but its use was not studied until after ether had proved itself. The oxide is now used only in dentistry and in a few minor surgical operations because of the weakness of the anesthesia produced and its short duration. *Chloroform* has been used

¹ A date after the name of a compound indicates the year when the compound was first used for the particular purpose mentioned.

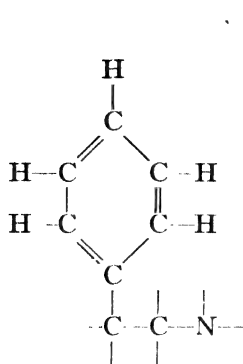
in the past for general surgery, but it is too toxic and has been largely replaced by other compounds.

There are several local anesthetics whose action is dependent upon the freezing by evaporation from tissue surfaces in a localized area. *Ethyl chloride* is sprayed on the skin; because of the low boiling point (13°) it evaporates and absorbs heat from the skin. The insensibility to pain persists for only a short time, and consequently ethyl chloride is useful only for minor operations such as the incision of boils. *Novocaine* has been the standard local anesthetic for over 25 years. It belongs to an entirely different class of compounds, and its action is related to the nervous system.

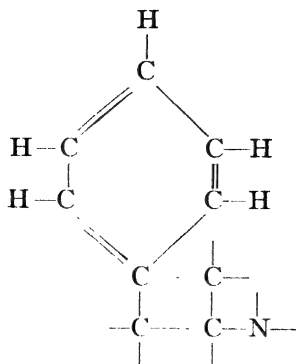


Sympathomimetics. The sympathomimetic compounds are those which have as their physiological action their ability to raise the blood pressure and to some extent cause excitation of the sympathetic nervous system. These compounds represent one of the earliest and most successful attempts to correlate pharmacological activity with chemical structure. The historical background for the sympathomimetic compounds centers in *epinephrine*, adrenaline, a hormone that was first isolated in 1895 and synthesized in 1904. With the elucidation of the structure of epinephrine a search was made for similar compounds

with modified characteristics. The net result of these investigations was the discovery that nearly all sympathomimetic compounds have either one or the other of the following closely related structures:



β -Phenylethylamine skeleton



Phenylisopropylamine skeleton

The particular characteristics of the compound are determined by the atoms or groups of atoms on the side-chain and to a lesser extent on the benzene ring.

Epinephrine is prepared commercially from the adrenal medula of cattle or by various synthetic methods. It is used to control hemor-

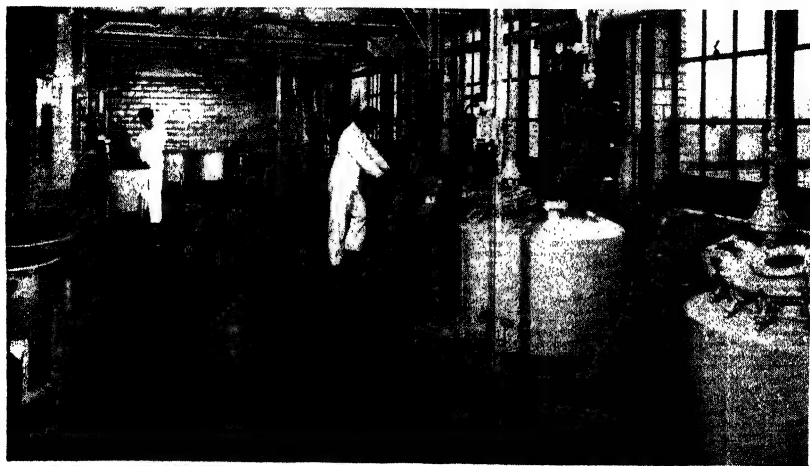
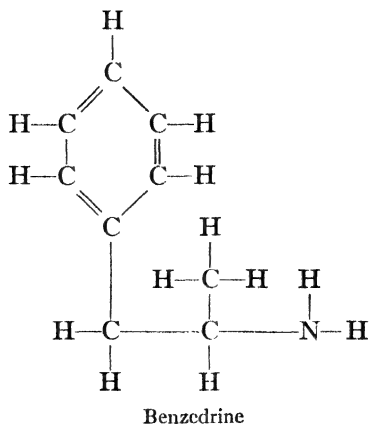
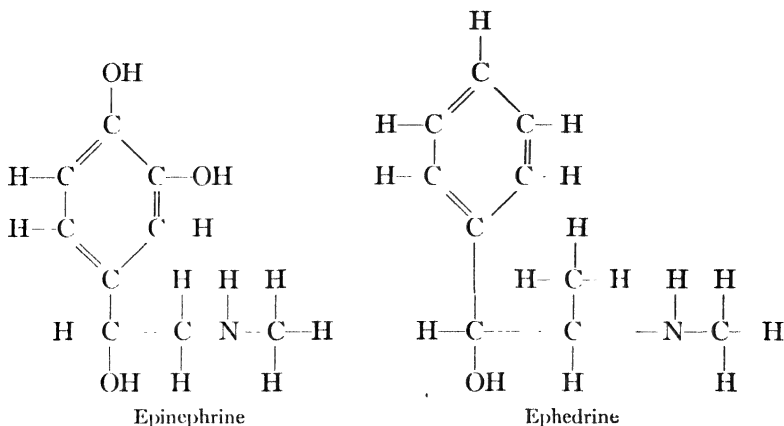


Figure 208. Insulin production in a modern pharmaceutical plant. Insulin is used by diabetics. (Courtesy of Eli Lilly and Company.)

rhages and to relieve nasal congestion. Epinephrine is often used in conjunction with a local anesthetic to prolong anesthesia by retarding circulation in the area involved. It is also used as the pharmacological standard for evaluation of other sympathomimetic amines.

Ephedrine was originally obtained from the Chinese herb mahuang but is now synthesized. It is used in the treatment of hay fever and other nasal disturbances and to prevent attacks of asthma. Ephedrine is also used to sustain blood pressure in spinal anesthesia.



Benzedrine is the simplest and best known of these compounds. It is widely used for relief of nasal congestion, sinusitis, hay fever, and

asthma. Benzedrine stimulates the nervous system and is used in the treatment of certain depressive conditions, but too much will cause excitement and an anxiety complex. Benzedrine should not be used indiscriminately, especially before and during periods of mental stress (such as final examinations).

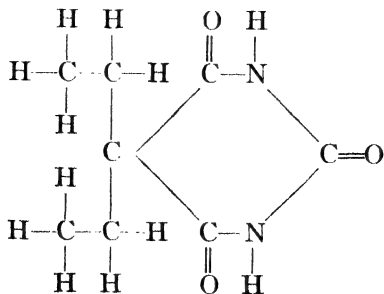
Several other types of compounds have also been used as *stimulants*, and *ethyl alcohol* is one of the best known but not necessarily the most desirable. Almost all of the effects of alcohol are caused by its action on the nervous system. The active ingredient of most tonics is alcohol (frequently in concentrations as high as 22 per cent or more).

Smelling salts are usually ammonium carbonate, $(\text{NH}_4)_2\text{CO}_3$, which decomposes slowly in the atmosphere to liberate ammonia, which is a heart stimulant.

Sedatives. For those who are already too excited there are a number of sedatives and soporifics. These compounds have the property of quieting the nerves and causing general relaxation. The soporifics (Latin *sopor*, a heavy sleep; *facere*, to make) cause one to sleep.

The oldest and still much used sedative is sodium bromide (NaBr). Its wide use as a yawn provoker is signified by the calling of any thrice-told tale "an old bromide."

The most popular soporifics belong to the family of compounds that consists of the substituted barbituric acids. The formulas for two of the common ones follow:



Veronal
(Barbital)

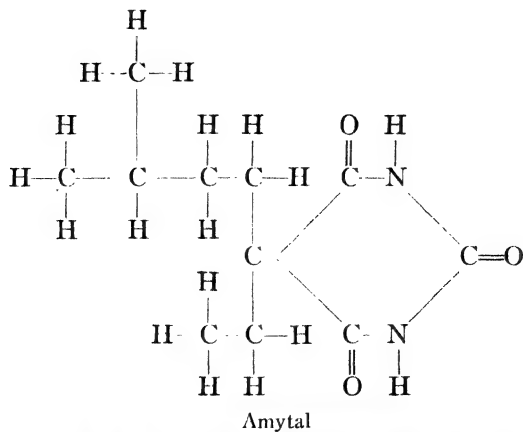
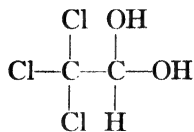


Figure 209. Preparation of influenza vaccine. (Courtesy of Parke, Davis & Company.)

Phenobarbital is similar to barbital but has one ethyl group replaced by a benzene ring.

It is almost impossible to take an overdose of sleeping pills “accidentally.”

Another compound that has been used in the past as a soporific and is still used indirectly for such purposes is chloral hydrate.

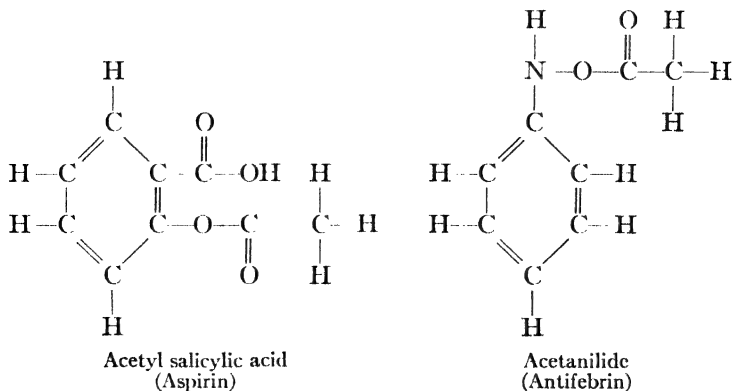


Chloral hydrate

It is the active ingredient in most "knockout drops" and "Mickey Finns."

Analgesics and Antipyretics. Analgesics are compounds that have the ability to relieve pain, while antipyretics reduce fever. Many compounds possess both properties and thus serve a dual purpose. The main difference between an analgesic and an anesthetic or soporific is that the former makes one insensible to pain while the latter merely makes one insensible.

The most famous of all analgesics is *aspirin*, which is also an antipyretic. Aspirin is produced to the extent of millions of pounds a year and sells for about fifty cents a pound. It is of interest to note that nearly all of the aspirin sold in this country is made by only three companies and that aspirin sold by a reputable company is the same as that sold by another reputable company regardless of the price per hundred tablets or the name stamped on the tablet. An aspirin tablet contains only a small amount of aspirin, and the remainder is filler that ranges in nature from clay or chalk to dextrose and mannose. The speed with which a tablet dissolves is dependent upon the filler and not the aspirin. The sodium salt of aspirin, sodium acetyl salicylate, is more soluble than aspirin but has the same physiological activity.



Acetanilide, Antifebrin, is another compound that is extensively used in headache powders for the relief of pain, and to lower fever. It is not so safe as aspirin, for it decomposes in the body to give aniline, which in turn destroys the red blood corpuscles. There are several other compounds, similar to acetanilide but somewhat less toxic, that are now used in the more expensive headache remedies; for example, *aminopyrine* and *antipyrine*.

The next time a headache powder is purchased, read the label and see what it contains; it may be less expensive to buy undiluted aspirin.

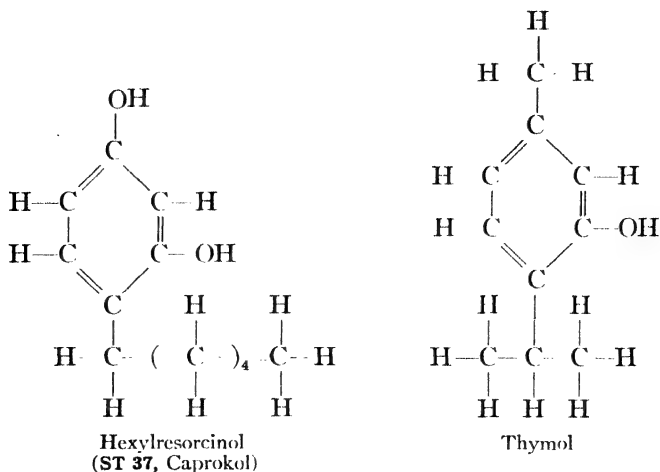
Morphine (Greek *Morpheus*, Greek god of dreams) is a compound used to relieve severe pain and is one of the most useful drugs known. It is a naturally occurring compound that constitutes about 10 per cent of opium and is its active ingredient. *Opium* is the dried juice from unripe seed capsules of certain varieties of poppy. When morphine is treated with acetic anhydride, *heroin* is formed; the methyl ether of morphine is *codeine*, a compound frequently used in place of morphine.

The use of morphine as an analgesic is restricted because it is habit-forming and because it gives one a feeling of euphoria. Several recently developed compounds are equal to morphine in potency but are free from some of its undesirable side reactions. They are marketed under various names such as Demerol and Methadon (Adanon, Dolophine, Amidone). *Methadon* is short for 6,6-dimethyl-4,4-diphenyl-3-heptanone. The structure of morphine is even more complex, and morphine may never be synthesized commercially. Methadon was developed in Germany during World War II.

Antiseptics. Next to aspirin, the antiseptics are perhaps the commonest and most accessible of the medicaments. If one believes what is written in advertisements, it would be impossible to be successful in any of the major activities without proper use of antiseptics, for they are frequently the active ingredients of mouthwashes, tooth pastes, anti-body-odor soaps, etc.

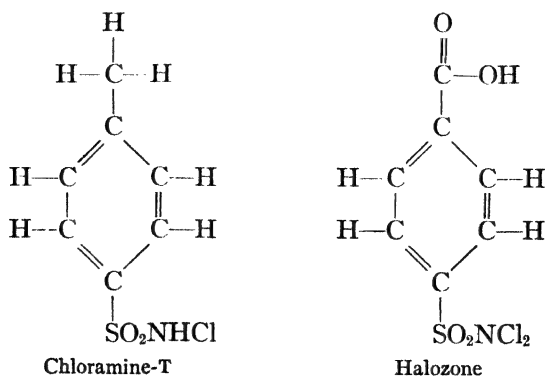
Phenol is the compound with which other antiseptics are compared to ascertain their relative effectiveness, although phenol itself is not a very potent or useful antiseptic. The use of *cresols* (hydroxy toluenes) as antiseptics has been mentioned previously. The marked increase in germicidal power and decrease in toxicity of cresols over phenol caused by the introduction of a methyl side-chain ($-\text{CH}_3$) stimulated research on the preparation of even better antiseptics. The result of

this research was *hexylresorcinol* (ST 37, Caprokol), which is used as a general antiseptic although it has an irritant effect on the skin.



Thymol is both the disinfectant and the flavoring agent in most mouthwashes and gargles. It is obtained from the oil of thyme.

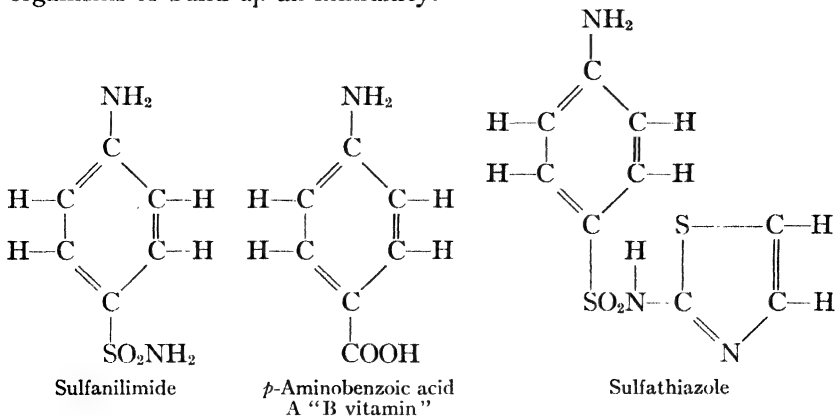
Chloramine-T is a compound that liberates hypochlorous acid (HClO) slowly on contact with water and is an effective antiseptic used in the treatment of wounds. The action is similar to that involved in the purification of water by the addition of chlorine; in each instance the active agent is hypochlorous acid. A closely related compound, *Halozone*, is pelleted with sodium carbonate and is used for the sterilization of drinking water on camping trips, etc.



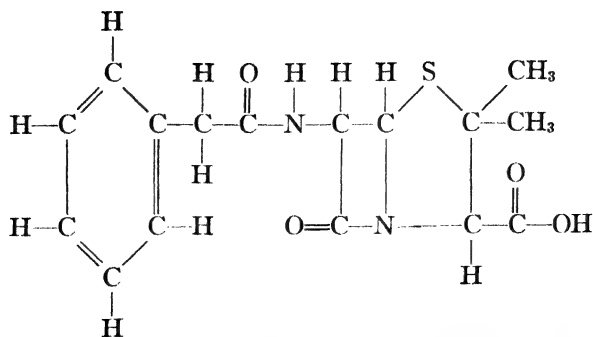
A number of mercury-containing dyes are used as antiseptics, *mercurochrome* being perhaps the most widely used and least effective. A more effective one is *merthiolate* (sodium ethyl mercurithiosalicylate), which although not fire-engine red in color still has sufficient color to please the more exacting child and parent. These dyes are generally sold in alcoholic solutions (*linctures*), and, at least in the case of mercurochrome, the alcohol is the antiseptic agent. A 3 per cent water solution of mercurochrome is worse than no treatment because of the false feeling of security it implants.

Antibiotics. A recent development in the treatment of disease and infection is the use of antibiotics. *Antibiotics* are compounds that resemble the vitamins in chemical structure but not in functions. These compounds, because of their similarity to vitamins, seem to enter into a specific catalytic system of an organism and then render it inoperative.

The first and still very important class of antibiotics is the *sulfa drugs* (1933). The sulfa drugs appear to act by replacing the similar *p*-aminobenzoic acid, a "B vitamin," in certain organisms and preventing them from growing. They are especially effective against certain types of bacteria, but excessive use of sulfa drugs will cause these organisms to build up an immunity.



Several naturally occurring antibiotic substances seem to function in a similar manner. The outstanding ones are *penicillin*, *streptomycin*, and *chloromycetin* from molds. Penicillin has been studied the most extensively, and its chemical structure has been determined.



Penicillin G

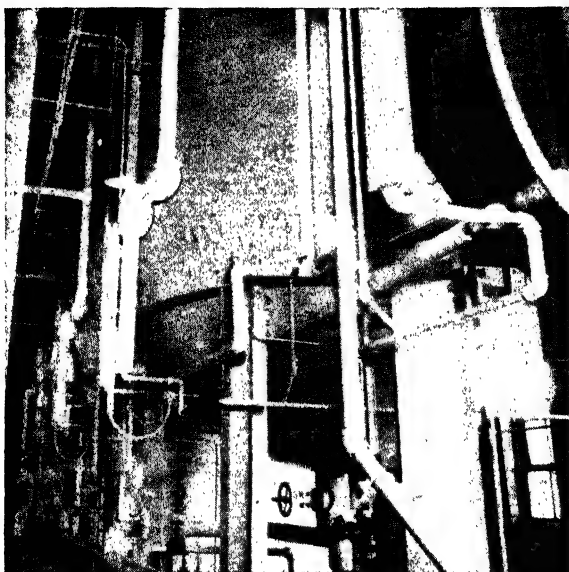


Figure 210. Large tanks used in the production of penicillin. (Courtesy of the Commercial Solvents Corp.)

Over 180 million dollars worth of penicillin was produced in 1947.

There is ample reason to believe that, as fuller details regarding catalytic systems and their functioning in various organisms are known, it will be possible to synthesize specific compounds to interfere with specific metabolic processes. As yet we have made only a beginning.

Considerable success has also been achieved by giving large doses of

various B vitamins to cause an acceleration of a metabolic process in the body that produces a substance to combat a specific infection. *p-Aminobenzoic acid* is now used to cure Rocky Mountain spotted fever, which heretofore was almost always fatal. *Folic acid* is used in the treatment of pernicious anemia. These are only two examples in a rapidly growing field of research and accomplishment.

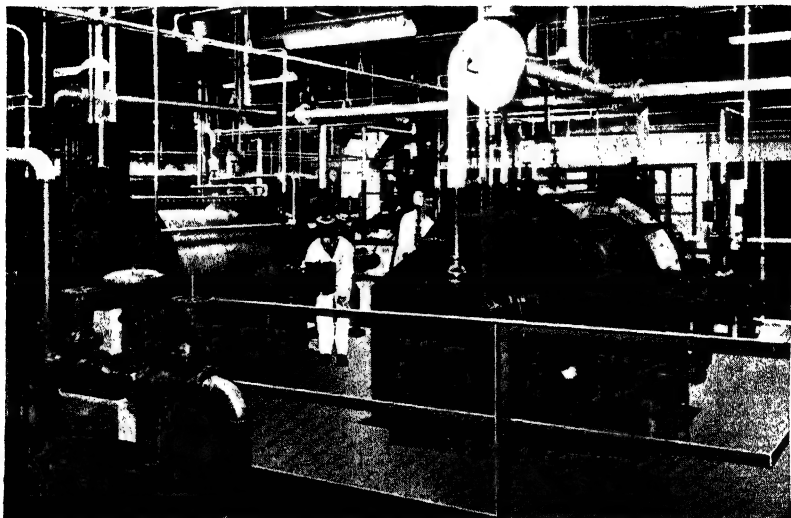
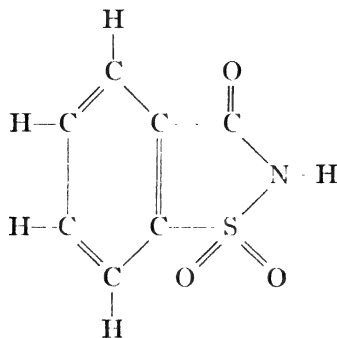


Figure 211. Rotary drum filters used in the removal of the mold from the penicillin fermentat on mixture. (Courtesy of Eli Lilly and Company.)

Miscellaneous Chemotherapeutic Agents. There are innumerable chemicals that could be mentioned, but space permits mention of only a few.

Antimalarial chemicals became of extreme importance during World War II because most of the early part of the war was fought in malarial areas. Before this time the only antimalarial used by the United States was *quinine* (first used in 1639), which was obtained from the bark of the cinchona tree grown on plantations in the Dutch East Indies. Extensive research during World War II resulted in the synthesis and testing of over 15,000 compounds, several of which show promise of being able to replace the German-developed atebtrin. *Atebrin* (1930) was the only antimalarial used clinically during the war as a substitute for quinine.

Saccharin (1879) is a compound about 500 to 600 times as sweet as table sugar; an aqueous solution retains a detectable sweet taste at a dilution of 1 to 100,000. It is used as a sweetening agent commercially and by diabetics who are incapable of tolerating sugar. It has no therapeutic power, but it does make the food more palatable.



Saccharin

EXERCISES

1. *New terms:* chemotherapy, sympathomimetic, analgesic, antiseptic, anesthetic, soporific, antipyretic, antibiotic.
2. What is the relationship between the use of ethyl chloride as a local anesthetic and the operation of a household refrigerator? Suggest another compound that might be used in place of ethyl chloride as a local anesthetic.
3. State to which type of sympathomimetic amine the following compounds belong: (a) benzedrine; (b) epinephrine; (c) ephedrine.
4. What is the difference between an analgesic and an anesthetic?
5. Wherein is the structure of chloral hydrate unique? (A suggestion: See the discussion of aldehydes, Chapter 26.)
6. Should one believe everything one reads in advertisements or hears over the radio pertaining to aspirin? Explain.
7. Name and give the formulas of three anesthetics closely related in structure.
8. Give an important use for and the formula of each of the following compounds: (a) nitrous oxide; (b) saccharin; (c) *p*-aminobenzoic acid; (d) ethyl chloride; (e) thymol; (f) novocaine.

9. Why is morphine dangerous to use as an analgesic?
10. List the natural sources of each of the following compounds: (a) ephedrine; (b) morphine; (c) cresols; (d) thymol; (e) penicillin.
11. What type of compounds was first studied in an attempt to correlate structure with physiological activity?
12. Why is it ill-advised to take benzedrine to stay awake all night studying before a final examination?
13. Give the formula of the compound used as the standard antiseptic; the standard sympathomimetic.
14. What is the danger associated with the use of acetanilide as an antipyretic?
15. Name and give the formula of one each of two different types of antiseptics.
16. What antimalarial was used as a substitute for quinine during World War II? Why was quinine essentially unavailable?
17. Is it necessary for a compound to have a complex structure to have physiological activity? Give three examples to support the answer given.
18. If there are 7000 grains in a pound, what is the cost of the aspirin in 100 five-grain tablets?

COLLATERAL READING

CONANT and BLATT: "The Chemistry of Organic Compounds," The Macmillan Company, New York, 1947, Chapter 32.

FIESER and FIESER: "Organic Chemistry" (abridged), D. C. Heath and Company, Boston, 1944, Chapters 24 and 33.

JENKINS and HARTUNG: "Chemistry of Organic Medicinal Products," John Wiley & Sons, Inc., New York, 1943.

SILVERMAN: "Magic in a Bottle," The Macmillan Company, New York, 1948.

WILLIAMS and HATCH: "An Introduction to Organic Chemistry," D. Van Nostrand Company, Inc., New York, 1948.

Chemistry and Agriculture

“Food will win the war and write the peace.” The position of agriculture has seldom been better stated than in this wartime slogan, for the soil and its products are a nation’s most valued possessions. In Chapter 29 mention was made that, either directly or indirectly, man is dependent upon plants for his food supply. Because of this dependency it has been predicted periodically that, with a fixed production of plant foods and an ever-increasing population, we face ultimate starvation. These prognostications are usually made without due respect for the three sciences upon which modern agriculture is based, plant breeding, chemistry, and engineering. The plant breeders are giving us better plants, while the chemist nourishes these plants, regulates their growth, and protects them from their many enemies. The engineers are ever busy increasing the efficiency of farming. The role of the chemist in agriculture may well become the most important, and his present achievements will be the subject of this chapter. There has been a remarkable increase within the last ten years in research and production of chemicals related to agriculture.

Chemicals for agriculture began in England in 1838 with the first use of the chemical fertilizers, superphosphate and ammonium sulfate. The fortune made by J. B. Lawes in this business was turned over, together with the ancestral estate of Rothamsted, to the British people. The first, and in many ways still the finest, of the world’s great agricultural experiment stations was thus founded on an agricultural chemical industry. Many chemical companies are at present supporting their own agricultural experiment stations (Fig. 212) because of their awareness that the farmer is their best customer.

The agricultural chemist actually works in one of two quite distinct directions: he finds either agricultural uses for chemical products or chemical uses for agricultural products. In recent years success in the former activity has been little short of sensational. There can now be produced 20 per cent more corn on 10 per cent fewer acres than in

1928, and 50 per cent more alfalfa is produced after one application of an insecticide. In 1946 so many potatoes were produced that they were used to make beverage alcohol or dumped in the ocean—the result of using chemicals that increased the yield of potatoes per acre by 50 per cent over the production per acre only three years previously.

The use of agricultural products as a source of chemicals, *chemurgy*,

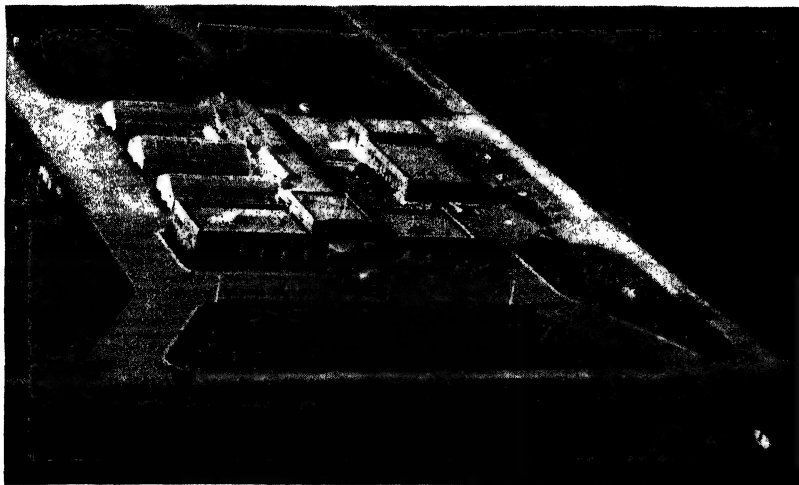


Figure 212. The West's largest laboratory and experimental farm devoted exclusively to the development of new and improved agricultural chemicals. (Courtesy of the Shell Oil Company, Inc.)

will be mentioned only briefly; for at present a relatively small fraction of our chemicals comes from this source, and many of the more important ones have already been noted (starch, dextrose, alcohol, etc.).

Fertilizers. Soil is composed of the degradation products of complex silicate rocks, sand, and the decomposing remains of vegetable life (*humus*). The soil has two distinct functions in relation to agriculture: it provides a secure anchorage for plants and trees, and it supplies all of the required plant food except carbon dioxide. In this latter function the soil frequently leaves something to be desired.

For a plant to enjoy a normal growth it must obtain from the soil a wide variety of chemicals, and it is not sufficient for these chemicals merely to be present in the soil—they must be present in a form suitable for plant utilization. Compounds of zinc, copper, boron, and manganese

are necessary, but only in very small amounts, for their action seems to be catalytic in nature. Magnesium, calcium, iron, silicon, and sulfur are also of importance, but their compounds are almost always present in sufficient quantities. Suitable compounds of *nitrogen*, *phosphorus*, and *potassium* are not present in most soils in sufficient quantities to support annual crops indefinitely. Compounds of "the big three" must be furnished to the soil in the form of fertilizers. *Fertilizers* are nutrients that are not present in the soil but are needed for plant growth.

*Classification of Fertilizers.*¹ The fact that so many different types of materials are used as fertilizers necessitates a somewhat involved scheme of classification. That which follows is typical:

- I. Direct fertilizer
 - A. Nitrogenous fertilizers
 - 1. Organic
 - a. Animal. Dried blood, tankage, fish scraps, manures
 - b. Vegetable. Straw, muck, peat, cover crops, cottonseed meal, etc.
 - 2. Inorganic (or mineral). Sodium nitrate, ammonium sulfate, ammonia, calcium cyanamide, etc.
 - B. Phosphate fertilizers
 - 1. Organic. Farm manures, guano
 - 2. Inorganic. Rock phosphate, superphosphate or acid phosphate, bones
 - C. Potash fertilizers
 - 1. Organic. Tobacco waste, farm manures, kelp
 - 2. Inorganic. Potassium chloride, potassium sulfate, wood ashes
 - D. Calcium fertilizers
 - 1. Inorganic. Quicklime, hydrated lime, limestone, gypsum
- II. Indirect fertilizer or amendment
 - A. Organic. Green cover crops, leaf mold, etc.
 - B. Inorganic
 - Calcium compounds, salt, iron compounds

Fertilizers in general may be classified as either of natural origin or commercial fertilizers. Although natural fertilizers are very important, the present discussion will be limited to commercial fertilizers. This is not a severe restriction, for the largest single outlet for chemicals

¹ Hedges and Brayton, "The Applications of Chemistry to Agriculture," Appleton-Century-Crofts, Inc., New York, 1938, Chapter IX.

is in the manufacture of fertilizer materials. During the 1947-1948 fiscal year over 18 million tons of commercial fertilizers was produced by 800 manufacturers. These fertilizers had a value of 400 million dollars. The value of fertilizers may be indicated in another way--about 20 per cent of the total crop production is the result of the use of fertilizers.

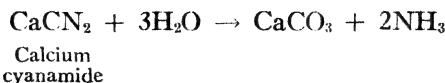
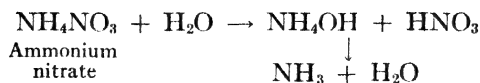
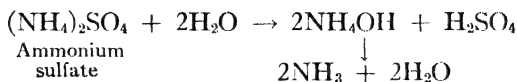
The *nitrogen-containing fertilizers* comprise by far the widest variety of compounds and are probably the most important. Table 21 lists some of the more important nitrogen fertilizers as well as the total for the phosphorus- and potassium-containing compounds produced during 1947-1948.

TABLE 21. Plant-nutrient Supplies, 1947-1948*

<i>Material</i>	<i>Tons of nitrogen</i>
Nitrogen imports:	
Sodium nitrate	102,080
Ammonium nitrate	33,125
Ammonium sulfate	20,327
Ammonium phosphate	14,518
Cyanamide	15,620
Calcium nitrate	1,650
Nitrogen domestic production:	
Ammonium sulfate	185,000
Ammonium nitrate	150,000
Sodium nitrate, ammonium phosphate, etc.	73,500
Solutions (liquid ammonia, etc.)	248,000
Organic (urea)	30,000
Total nitrogen in nitrogen fertilizers	873,820 tons
Total P ₂ O ₅ in phosphate fertilizers	1,900,000 tons
Total K ₂ O in potassium fertilizers	1,000,000 tons

* From a table in *Chemical and Engineering News*, 26, 19 (1948).

Nearly all of the important nitrogen fertilizers are compounds that react with the moisture in the soil to produce ammonia that is utilized by the plant.



Ammonium sulfate is an inexpensive fertilizer because the compounds from which it is prepared (ammonia and sulfuric acid) are inexpensive and also because it is a by-product of the manufacture of coke and of certain operations in the petroleum industry. The sulfuric

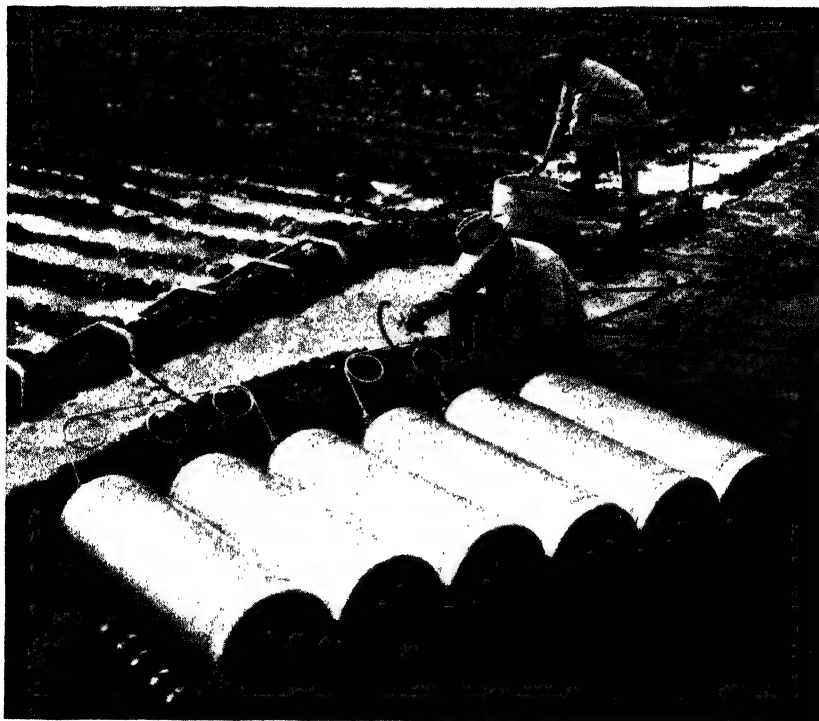


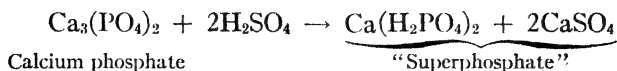
Figure 213. Nitrogen, essential to plant growth, is metered out of cylinders in the form of ammonia directly into the irrigation system. The process is called nitrogenation and is in widespread use in the West. (Courtesy of the Shell Oil Company, Inc.)

acid formed when ammonium sulfate hydrolyzes in the soil makes the soil acid (sour) and necessitates *liming* the soil with slaked lime or finely ground limestone, which neutralizes the acid.

Urea and cyanamide are more desirable because they give non-acid hydrolysis products, but they are more expensive. Ammonium nitrate has the distinct advantage of having nitrogen present in both parts of the molecule. Since World War II large quantities of ammonium nitrate have been recovered from explosives.

A recent development in the use of fertilizers is the addition of anhydrous ammonia directly to irrigation water (Fig. 213) or to the soil (Fig. 216) in dry farming. This method holds great promise.

There is only one *phosphorus-containing fertilizer* used extensively, and that is *superphosphate*, prepared by treating the naturally occurring insoluble calcium phosphate with sulfuric acid.



This calcium acid phosphate is water-soluble, and the phosphorus is thus made available to the plant. Calcium phosphate is obtained from Florida and Tennessee, and there are very large reserves in Idaho and Montana. The amount of phosphate rock mined in 1947 was nearly 5 million tons. The phosphorus content of a fertilizer is recorded as P_2O_5 .

The two *potassium-containing fertilizers* are potassium chloride and sulfate. These compounds are obtained from Searles Lake, Calif., and Carlsbad, N.M. Searles Lake is not a lake but a bed of crystallized salts about 12 square miles in area and 60 to 70 feet deep. The New Mexico deposits are about 1000 feet underground and contain potassium chloride.

Hydroponics. It has been mentioned that the role of soil in plant growth is twofold—it furnishes both the nutrients and the support for the plant. As far back as 1699 it occurred to an Englishman by the name of John Woodward that with proper support plants could be grown without soil by letting water supply the various plant foods needed. He used river and spring water, and his experiments met with indifferent success. In 1859 the German Knop improved on the original idea by adding certain chemicals to the water. The soilless growth of plants remained with the scientist until recently, when it was glamorized with the name *hydroponics* (nutriculture) and became the hobby of many.

Hydroponics is not as simple as it may seem at first glance because of the difficulty of maintaining a proper balance of all the various compounds needed for normal growth. A typical formula for a solution to be used for the soilless growth of plants contains, per 100 gallons of water, 9 oz. of calcium nitrate, 9 oz. of potassium nitrate, 3 oz. of magnesium sulfate, 2 oz. of diammonium hydrogen phosphate, and

very small amounts of iron tartrate, manganese chloride, phosphoric acid, and zinc sulfate. The concentrations of all of these compounds must be adjusted frequently during the growing season; the results are sometimes worth the effort. There have been reported tobacco plants 20 feet high and yields of tomatoes of 217 tons per acre compared with 5 tons per acre in the field.

During and after World War II hydroponics supplied many a barren outpost with its vegetables and at a cost only slightly more than that of imported vegetables. During the 1946-1947 season the Army grew 3,580,000 pounds of vegetables by hydroponic methods. The largest single installation contains over 100,000 square feet of hydroponic beds and is located at Chofu, Japan.

Some feel that the world's food problems may be solved by hydroponics because it will enable nations with dense populations and little agricultural land to grow their own food.

Economic Poisons. It is not sufficient for the chemist to furnish the farmer with better fertilizers to increase the yield per acre; he must also furnish him the means of protecting these crops from a host of biting, chewing, and sucking insects. There are 80,000 different kinds of insects in North America, at least 5000 of these having economic importance. Research and test work are under way toward finding methods of controlling about 200 of them.

In addition to the insects and their relatives there are also plant diseases and weeds to be considered. In the United States there are 25,000 infectious plant diseases, of which 10,000 are of known economic importance. Even after the produce has been harvested, the battle has not been won unless the produce is protected against mildew, rot, and rats. There are an estimated 200 million rats, each of which eats a bushel of grain a year.

The loss due to insects in a typical year for a few selected crops is indicated in Fig. 214. The total loss has been estimated as 2 billion dollars by insects and another 2 billion dollars by various plant diseases. Real progress in combating this loss has been made only in the last ten years with the development of many new organic and inorganic compounds—economic poisons. The production of these chemicals is now a 50-million-dollar industry.

Insecticides. Insecticides are generally classified according to the feeding habits of the insects associated with them. There are three main classes.

Before World War II nearly all of the insecticides were inorganic compounds, of which arsenicals (1869), fluorine compounds, and cyanides were the most important. The organic compounds used were mainly pyrethrum, rotenone (1911), and nicotine (*ca.* 1650), all of which come from natural sources. Various petroleum fractions (1875) and several nitrated phenols and *p*-dichlorobenzene were also used.

Dichlorodiphenyltrichloroethane (**DDT**) is the compound that has variously been described as the outstanding synthetic organic insecticide developed up to 1940 and as the wonder chemical of the age. It was the first of the new organic insecticides and launched the intensive search for other compounds even more potent. These researches resulted in the discovery of *Chlorodan* (**1068**), an octachloromethanotetrahydroindane, dichlorodiphenyldichloroethane (**DDD** or **TDE**), chlorinated camphene, benzene hexachloride (**666**, gammexane, **BHC**), tetraethyl pyrophosphate, and dinitro-*o*-cresol (**DNOC**). Each has its particular advantages and specific action. For example, the pyrophosphates are effective against aphids and mites, while **DDT** is particularly useful in killing leaf hoppers and mosquitoes. Benzene hexachloride is more effective than **DDT** against ticks; dinitro-*o*-cresol is the most efficient insecticide against grasshoppers.

These compounds seem to kill in a manner similar to the way antibiotics kill germs (Chapter 29). Because of their antibiotic action, it is possible to develop insects that are resistant to relatively large doses of a particular insecticide. There have already been propagated **DDT**-resistant flies. Against this type of resistance there is nothing to do but discover a new compound to take the place of the old, and then another, and so on.

Even if the insects do not develop an immunity to an insecticide, there are often other factors to frustrate the farmer. Consider the case of the apple tree. An apple tree may have three species of insects—codling moth (parents of the worm in the apple), aphids, and lady beetles. The codling moth larvae eat the apple, the aphids suck juices from both the apples and the leaves, while the lady beetles, being ladies, eat only the aphids. The tree is sprayed with **DDT**, and the moths are killed, but so are the lady beetles. The aphids are no longer eaten, and hence the balance of nature is disrupted and the tree is soon covered with aphids all busy sucking juices from it. The chemist comes to the rescue with a compound that kills aphids. At last the

orchardist can relax and count his profits—until a **DDT**-resistant codling moth develops.

It is still an interesting race to see who will inherit the earth—man or insect.

The use of insecticides is not, of course, restricted to the protection of plants. They are used to make both man and animal happy or at

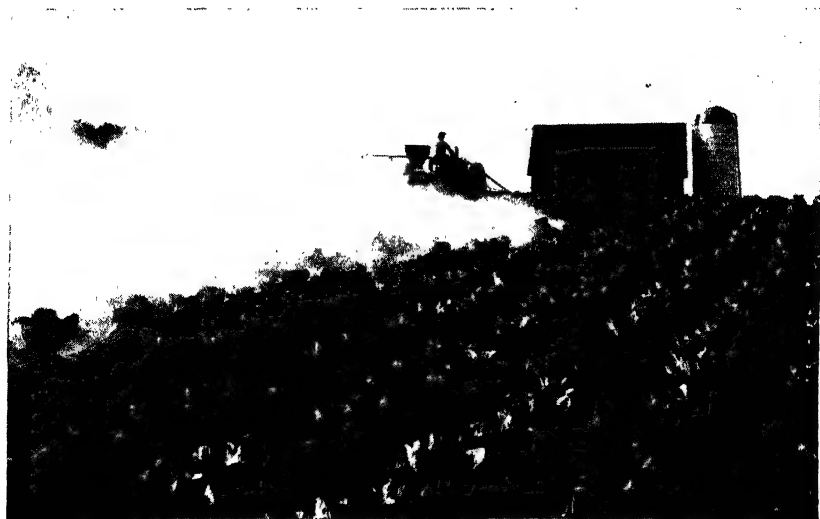


Figure 215. Dusting a cabbage field with an insecticide. (*Courtesy of the Standard Oil Co. of New Jersey.*)

least more contented. Steers gain up to 50 pounds extra and cows give up to 20 per cent more milk because of insecticide sprays. Bathing beaches, etc., are now sprayed to kill sand fleas, flies, mosquitoes, black flies, and the like—in fact, almost everything but bar flies. Because these insecticides are effective at very low dosages, it is economical to spray land of low productive value such as field-crop (Fig. 215), pasture, and range land, forests, and mosquito-breeding swamps. They are applied by the *aerosol* method (Chapter 14).

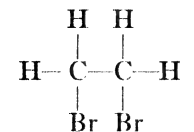
Insect Repellents. It is frequently desirable to use an insect repellent rather than an insecticide, especially in the open, where it would be impossible to kill all of the winged pests for miles around. During World War II several organic compounds were discovered for which various insects have an aversion. One of the most successful repellents

is a mixture of dimethyl phthalate, Indalone (*n*-butyl-6,6-dimethyl-5,6-dihydro-1,4-pyrone-2-carboxylate), and Dimelone [dimethyl-*cis*-bicyclo(2,2,1)-5-heptene-2,3-dicarboxylate]. Dimethyl phthalate alone is a good mosquito repellent and is usually the predominant material in compounded repellents. After looking at the chemical names of Indalone and Dimelone one might agree with the insects as to the repulsive natures of these compounds.

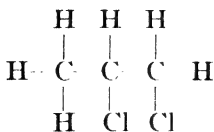
Fumigants. The simple operation of raising a good crop does not mean that the troubles of the farmer are over. There are many misfortunes that can befall such crops as tobacco and grains, which are stored for long periods of time. About 5 per cent of the annual grain crop is lost during storage. To protect stored material from both plant and animal attack, the materials are fumigated.

As a class, the low-molecular-weight halogenated paraffin hydrocarbons and olefins are generally effective against a variety of pests. For example, grains are fumigated with carbon tetrachloride and ethylene dichloride.

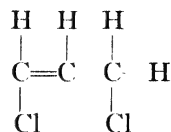
One of the greatest agricultural chemical developments has been in the field of soil fumigation. Control of nematodes, which has been the limiting factor in agricultural production in all the tropical and most of the temperate areas of the world, is being accomplished cheaply and effectively by the direct injection of fumigants into the soil (Fig. 216). The fumigants most frequently used are ethylene dibromide and a mixture of dichloropropane and dichloropropene called **D-D**.



Ethylene dibromide
B.p., 132°



Propylene dichloride
B.p., 97°



1,3-Dichloropropene
B.p., 104-112°

Plant Disease. Less progress has been made in combating plant disease than in any other phase of agriculture; nevertheless some progress has been made. The older copper and sulfur sprays are being replaced by quaternary ammonium compounds, naphthoquinone, and other synthetics. These materials are effective in concentrations as low as 4 ounces to 100 gallons of water where as much as 10 pounds of copper compounds would be required. The quaternary ammonium

salt, **CETAB** (cetyl trimethyl ammonium bromide), for example, is said to be a bactericide, germicide, fungicide, deodorant, and dispersing and wetting agent. These compounds will apparently do almost anything but plow a straight furrow. Zinc ethylene *bis*-dithiocarbamate is effective against potato and tomato blight, which in 1946 caused a loss of 50 million dollars worth of tomatoes.

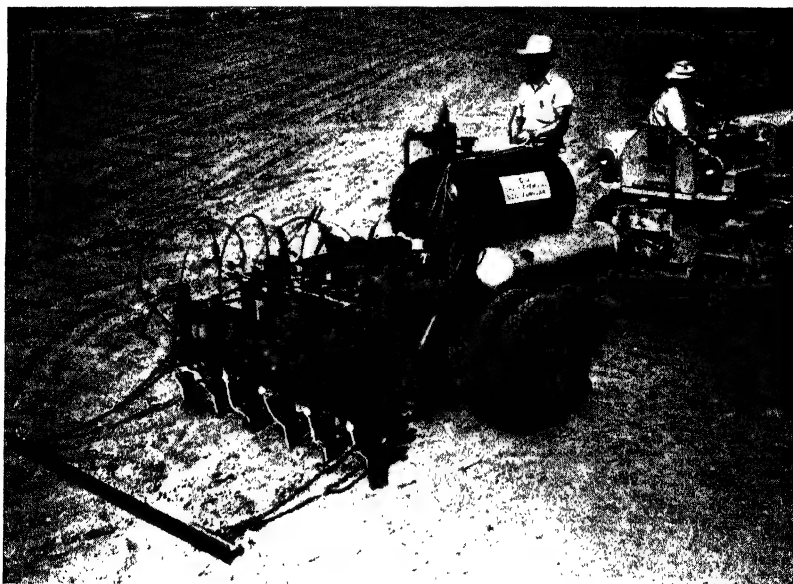


Figure 216. The simultaneous addition of the soil fumigant **D-D** and ammonia. (Courtesy of the Shell Oil Company, Inc.)

Plant-growth Regulators - Plant Hormones. Plant-growth regulators, commonly called *plant hormones*, are another example of chemistry's contribution to agriculture. There seems to be no limit to the magic that can be accomplished with these materials. They are used to kill weeds, to prevent apples and pears from dropping prematurely, to produce uniform crops of seedless tomatoes, to prevent the sprouting of potato tubers in storage, to stimulate uniform flowering and ripening of pineapples, and to regulate the date of flowering of some fruits.

More money is spent by the farmer in controlling weeds than all the other crop pests. For many years weeds and vegetation in general

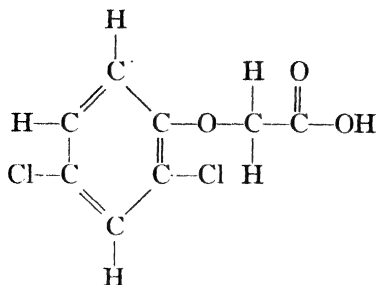
have been controlled to some extent by the use of sodium chlorate, sodium arsenite, and borax. Special petroleum oils are used for general herbicides, especially on roadsides, ditchbanks, and airport and factory grounds.

The recent development of plant hormones, however, has opened up new vistas for the farmer. These compounds seem to work in a manner somewhat similar to that of the newer insecticides; they enter into the

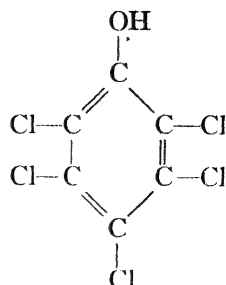


Figure 217. Rye field 10 days after a portion (left) had been sprayed with **2,4-D**. (Courtesy of the Buffalo Turbine Agricultural Equipment Co., Inc.)

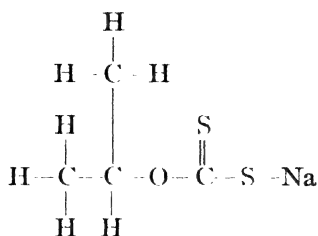
metabolic processes of the plant and disrupt them, causing death and destruction. The most efficient weed killer is 2,4-dichlorophenoxyacetic acid (**2,4-D**), which in minute quantities (as little as one-half a gram per acre) stimulates the broad-leaved plants to greater growth but in slightly larger amounts overstimulates the plant and causes death. **2,4-D** will kill only the broad-leaved plants and therefore can be used to kill weeds in lawns, grainfields (Fig. 217), and pastures. On the other hand, isopropyl-N-phenyl carbamate and allyl mixed chlorophenyl carbonate will kill grass, and sodium isopropyl xanthate will kill all types of plants. A mixture of **2,4-D**, pentachlorophenol, and an aromatic oil is a very potent weed killer.



2,4-Dichlorophenoxyacetic acid
2,4-D



Pentachlorophenol



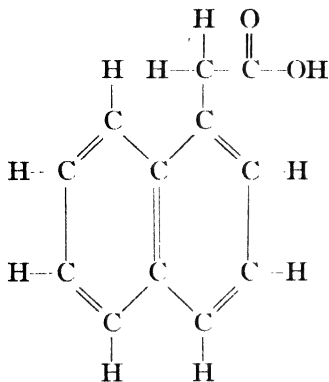
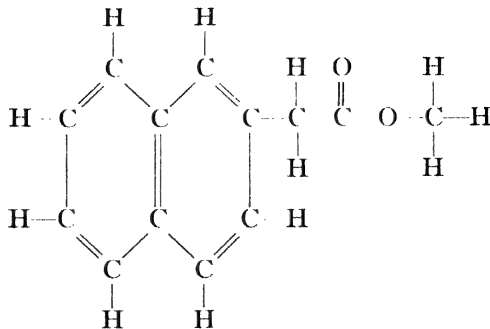
Sodium isopropyl xanthate

Both sodium isopropyl xanthate and calcium cyanamide are used as defoliant for cotton to permit easier picking, especially when machinery is used.

All the weed killers of the plant-hormone type are slow in action and must be used during the growing season for best results. It usually takes a week or ten days for the weed to die, but when it dies it dies all over—never to come up again from a root still alive.

The use of plant hormones to regulate growth is also of great importance. 3-Indolyl acetic acid and *alpha*-naphthalene acetic acid are used in promoting root growth on cuttings and transplanted plants and to prevent apples and pears from dropping before they have matured. The methyl ester of *beta*-naphthalene acetic acid when applied to potatoes when they are put in storage prevents sprouting and water loss. Ethylene has hormone-like properties and will cause the ripening of fruits while in storage. Formulas representing two plant hormones are shown on page 518.

In this discussion of chemicals used by agriculture there has been space to mention only a few of the many compounds. The selection has been in some cases rather arbitrary, but the general philosophy has

*Alpha*-naphthalene acetic acidMethyl ester of *beta* naphthalene acetic acid

been to give an over-all picture with only a relatively small amount of detail. Many trade-named products have been left out, and many of the different trade names of the compounds mentioned have been omitted. It is impossible to give all of the trade names of some of the more popular agricultural chemicals. In California alone there were more than 50 different producers of DDT in 1947 with each using his own trade name for it.

Table 22 gives the consumption in 1947 of some of the more important economic poisons.

TABLE 22. Estimated Consumption of Economic Poisons in 1947*

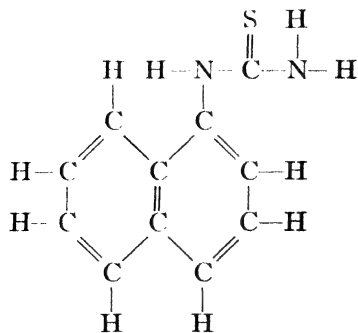
<i>Material</i>	<i>Pounds</i>
Calcium arsenate.....	35,000,000
Lead arsenate	28,000,000
Copper chemicals (sulfate base)	105,000,000
Paris green	1,000,000
Rotenone	8,000,000
Pyrethrum	5,000,000
Sodium fluoride	4,000,000
Sodium fluorosilicate	3,000,000
Thiocyanates.....	7,500,000
Formaldehyde.....	1,750,000
DDT and homologues	25,000,000
Benzene hexachloride	5,000,000
2,4-Dichlorophenoxyacetic acid.....	5,000,000
Diphenylamine.....	200,000
Phenothiazene.....	4,000,000
Carbon disulfide	5,000,000
Carbon tetrachloride.....	6,000,000
Ethylene dichloride	6,000,000

* Chemical Division, Bureau of Foreign and Domestic Commerce.

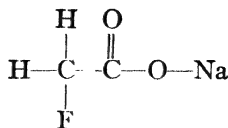
Rats. The rat is a greater factor in our lives than most people realize. Rats are the most harmful, the most destructive, the most menacing to human health of all the animal pests. Their annual cost to this country is about 400 million dollars. They transmit to man a formidable array of diseases, including bubonic plague, typhus, spirochetal jaundice, ratbite fever, food poisoning, tularemia, rabies, and trichinosis. Rats often kill for the joy of killing; they kill chickens, ducks, baby pigs, lambs, and human beings. They damage property by gnawing, which causes floods and fires.

From the preceding statements it should be evident that the term *rat* when applied to human beings should be used advisedly.

Recently there has been discovered a highly specific poison for the brown rat—the common rat of the United States. This compound, **ANTU** (*alpha*-naphthylthiourea), is relatively non-poisonous to other rodents and animals and, so far as is known, non-toxic to man except in large amounts. **ANTU** kills through the stomach, usually within 10 to 24 hours.



Alpha-naphthylthiourea
ANTU



Sodium monofluoroacetate
1080

Sodium monofluoroacetate (**1080**) is another widely used rodenticide. It is extremely poisonous to most animals and can be purchased only by qualified exterminators.

Within the next few years there should be a definite decrease in the damage done by rats if these two chemicals are used extensively.

Chemurgy. Thus far in this chapter the emphasis has been placed upon the use of chemicals by agriculture. An equally interesting development in recent years has been the increasing use of agricultural products as a source of chemicals—*chemurgy*. The type of materials

that can be grown on farms are mainly starch, cellulose, protein, and vegetable oils, and it is with these materials that most of the work has been done.

A pioneer in the field of chemurgy was the Negro scientist George Washington Carver (*ca.* 1864–1943, Fig. 218), late of Tuskegee Institute. Through the efforts of Doctor Carver the southern farmer diversified his crops and produced large quantities of peanuts and sweet

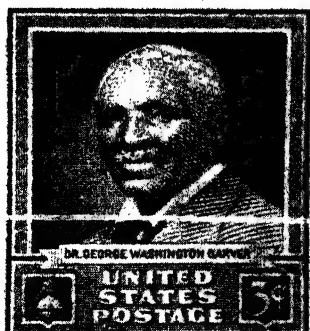


Figure 218. Dr. George Washington Carver, to whom the Southern farmers owe much.

potatoes. When these crops were overproduced, he developed uses for them other than as food. Peanuts were made to yield such widely divergent end products as cheese, coffee, ink, dyes, soap, and insulating board; a total of over 300 different products was made. The sweet potato proved to be equally versatile and provided vinegar, flour, molasses, rubber, etc. Of course, very few of these products could compete with similar materials from other sources, but this research laid the foundation for modern chemurgy and gave it the impetus to achieve its present eminence.

The many facets of chemurgy are illustrated by some of the achievements of 1947, which range from using protein (zein) from corn for phonograph records to vitamin C from English walnut hulls for the frozen-fruit industry. The lowly corn cob was made to yield furfural, which in turn was used to manufacture nylon; one bushel of corn cobs will make 40 pairs of nylon stockings. Shelled peanuts are being made into fibers, and pectin from citrus peels is used to make casings for sausages, cheese, and other products. Fifteen companies are extracting rutin from buckwheat to use in the treatment of capillary fragility.

The soybean is the most widely used farm product for chemurgical purposes. Soybean glue has been used by the plywood industry since 1937, and the annual consumption is about 50 million pounds. Soybean protein is also used in paper coating, paper sizing, water paints and fire-extinguisher compound, textile sizing, bookbinding, sandpaper adhesive, match-head binder, etc.

Much of the research on chemurgy is being carried on at the four Regional Research Laboratories maintained by the United States Department of Agriculture and located at Philadelphia, Pa.; Peoria, Ill.; New Orleans, La.; and Albany, Calif.

EXERCISES

1. *New terms*: chemurgy, fertilizer, nutriculture, insecticide, fumigant, hydroponics, economic poison, insect repellent, plant hormone.
2. What chemical reaction of importance to agriculture do the following compounds have in common: ammonium sulfate, urea, and ammonium nitrate?
3. Write the formula of and give an important use for each of the following compounds: (a) dimethyl phthalate; (b) carbon tetrachloride; (c) ethylene dichloride; (d) methyl ester of *beta*-naphthalene acetic acid; (e) sodium monofluoroacetate; (f) ethylene.
4. What is the chemical name of (a) **DDT**; (b) **BHC**; (c) **DNOC**; (d) **ANTU**; (e) **2,4-D**?
5. What are the two primary functions of the soil in relation to plant growth? Can plants be grown without soil? Explain.
6. Write an equation for the preparation of ammonium sulfate from sulfuric acid and ammonia. Give two reasons why ammonium sulfate is inexpensive.
7. What chemical is credited with instigating the present intensive investigations pertaining to organic insecticides?
8. What type of compound is frequently used as a fumigant? Would these compounds be expensive? Explain.
9. Why was there a very large quantity of ammonium nitrate available for use as a fertilizer after World War II?
10. What are two drawbacks to the use of the modern antibiotic type of insecticides?
11. What three elements are usually added to the soil in the form of their compounds?
12. List five different uses of soybean protein.
13. Classify insecticides according to the feeding habits of the insects associated with them.
14. Give a broad general classification of fertilizers.

15. What are "economic poisons"? Name five.
16. List seven metallic elements and two non-metallic elements the compounds of which are necessary for the normal growth of plants and which are usually present in the soil in sufficient quantities.
17. Who may be considered the father of modern chemurgy?
18. Give the formula of the principal phosphorus-containing fertilizer. Give the formulas of the two main potassium-containing fertilizers.
19. Give the location of the four Regional Research Laboratories of the United States Department of Agriculture.
20. What was the average cost per pound of the commercial fertilizers produced in the 1947-1948 fiscal year?
21. How many tons of ammonium sulfate are represented by 874,000 tons of nitrogen?

COLLATERAL READING

COLLINGS: "Commercial Fertilizers, Their Sources and Use," The Blakiston Company, Philadelphia, 1947.

CROCKER: "Growth of Plants," Reinhold Publishing Corporation, New York, 1948.

DETHIER: "Chemical Insect Attractants and Repellents," The Blakiston Company, Philadelphia, 1947.

ELLIS and SWANEY (revised by Eastwood): "Soilless Growth of Plants," Reinhold Publishing Corporation, New York, 1947.

Plastics and Resins.

Paint, Varnish, and Lacquer

IT HAS BEEN the custom of man to name a period in history for its predominant influence or achievement. Thus we recognize the Bronze Age, the Iron Age, the Age of Elizabeth, and many others. Hindsight being clearer than foresight, it is relatively easy to pick out a major influence of a past age but much harder to characterize a current period in history. Until the advent of nuclear fission, our times were rather optimistically referred to by some as the Plastics Age. Although there are many who would deny plastics this honor, there is none who would contend that the role played by plastics has been insignificant.

Plastics and resins are everywhere: in the car, the radio, in every room in the house. The present-day inexpensive but complicated toys would not be possible if it were not for plastics. By their very color, plastics make life a bit gayer. Paints, varnishes, and lacquers also add their share to man's well-being from both the practical and the aesthetic point of view. A familiar advertising slogan implies that if you save the surface you save all.

PLASTICS AND RESINS

There is no sharp line of demarcation between resins and plastics, and the terms are to a certain extent used interchangeably. A *plastic* is a relatively tough substance of high molecular weight that usually becomes soft enough when heated to mold under pressure. *Resins* are generally of lower molecular weight and cannot be molded. Those materials which soften on reheating are known as *thermoplastics*, and those which upon heating set to a non-softening material are called *thermosetting* resins.

TABLE 23. Synthetic Plastics and Resins

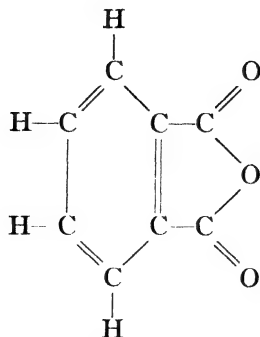
Thermoplastics

<i>Type</i>	<i>Monomer</i>
Cellulose acetate	
Ethenoid plastics:	
Polythene	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}=\text{C}-\text{H} \end{array} \quad (\text{Ethylene})$
Polystyrene	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{C}=\text{C}-\text{H} \\ \\ \text{C} \\ // \quad \backslash \\ \text{H}-\text{C} \quad \text{C}-\text{H} \\ \quad \quad \\ \text{H}-\text{C} \quad \text{C}-\text{H} \\ // \quad \backslash \\ \text{C} \\ \\ \text{H} \end{array} \quad (\text{Styrene})$
Polyvinyl	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}=\text{C}-\text{Cl} \end{array} \quad (\text{Vinyl chloride})$
	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{O} \quad \text{H} \\ \quad \quad \quad \\ \text{H}-\text{C}=\text{C}-\text{O}-\text{C}-\text{C}-\text{H} \\ \\ \text{H} \end{array} \quad (\text{Vinyl acetate})$
Polyacrylic esters	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{O} \quad \text{H} \\ \quad \quad \quad \\ \text{H}-\text{C}=\text{C}-\text{C}-\text{O}-\text{C}-\text{H} \\ \\ \text{H} \end{array} \quad (\text{Methyl acrylate})$
	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \quad \text{O} \quad \text{H} \\ \quad \quad \\ \text{H}-\text{C}=\text{C}-\text{C}-\text{O}-\text{C}-\text{H} \\ \\ \text{H} \end{array} \quad (\text{Methyl methacrylate})$

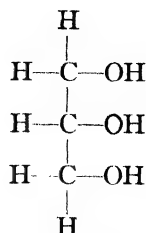
Thermosetting Resins

Type
Glyptal (alkyd)

Reactants

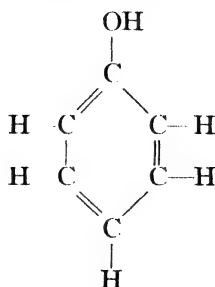


Phthalic anhydride

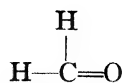


Glycerine

Phenol-formaldehyde

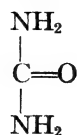


Phenol

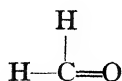


Formaldehyde

Urea-formaldehyde

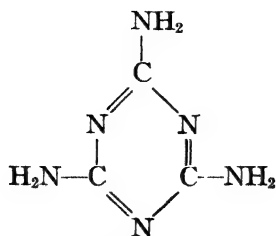


Urea

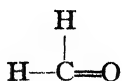


Formaldehyde

Melamine-formaldehyde



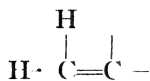
Melamine



Formaldehyde

Natural resins are of both vegetable and non-vegetable origin. The vegetable resins often occur as exudates from fir or pine trees—rosin (colophony), copal, sandarac, and dammar. *Shellac* is the common resin of non-vegetable origin and is a substance secreted by the lac insect (the female lac, no doubt). The modern synthetic resins are not only used as substitutes for the natural resins but also have found much wider application because of their greater adaptability.

Thermoplastics. Nearly all of the thermoplastic materials are made by polymerizing compounds that contain a terminal double bond.



Plastics made from compounds of this type are characterized by the fact that they will not undergo further reaction when heated (molded) but instead become soft and pliable. The synthetic rubbers previously mentioned (Chapter 26) have these same characteristics and are sometimes called elastoplastics.

High-boiling liquids are frequently incorporated with elastoplastics to keep them plastic, flexible, and tough at ordinary temperatures. These additives are called *plasticizers*, and the common ones are dibutyl phthalate and tricresyl phosphate, $(\text{CH}_3\text{C}_6\text{H}_4)_3\text{PO}_4$.

Celluloid is made from pyroxylin (Chapter 29), and it is the oldest synthetic plastic (1877). Pyroxylin alone is tough and brittle, and it cannot be molded; but when 2 to 20 per cent camphor is added as a plasticizer (Fig. 219), the material becomes thermoplastic. Celluloid is used to manufacture combs, brushes, containers, and photographic film. When pigments are incorporated in the clear plastic, it can be made to simulate tortoise shell, amber, malachite, and many other naturally occurring materials. Celluloid has the disadvantage of being highly flammable and of giving off toxic fumes when it burns.

The primary use of *cellulose acetate* is in the manufacture of textile fibers, but it is also used in the form of thin sheets for photographic film. Because film of this type is relatively non-flammable, it is called *safety film*. Cellulose acetate butyrate is used where a low-cost, tough material is desired. It is used for football helmets, telephone bases,



Figure 219. Pyroxylin being added to a mixing machine where it will be mixed with camphor and solvents. (*Courtesy of E. I. duPont de Nemours & Co.*)

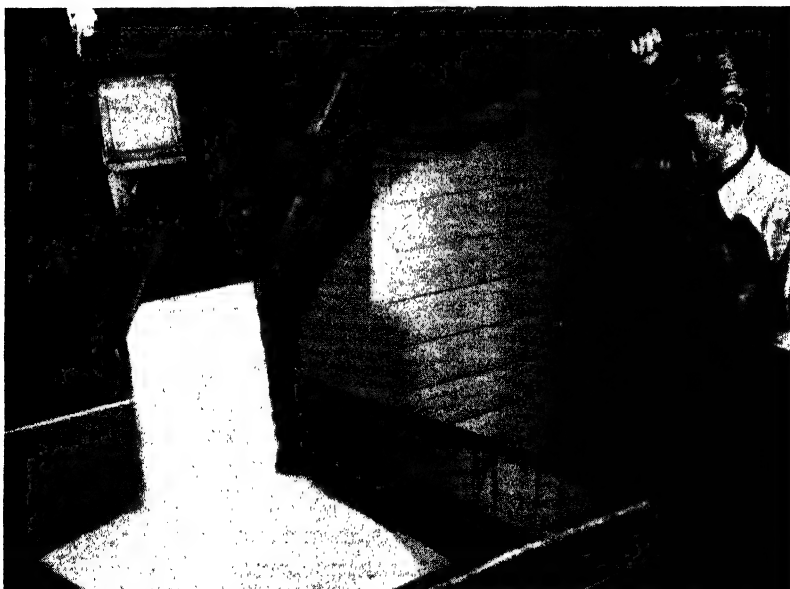


Figure 220. Ethyl cellulose — one of the toughest of all plastic materials. (*Courtesy of the Hercules Powder Co.*)

and toilet seats. The various ethers of cellulose (Methocel, 1939, and Ethocel, 1935) are used to some extent for films and molded or extruded objects, such as practically unbreakable toys, golf-club heads, hearing aids, and refrigerator parts. The nose of the famous proximity fuse of World War II was made of ethyl cellulose.

Polystyrene resins have been known since 1839, but they were not produced successfully in this country until 1937. They are used to make many novelty objects such as costume jewelry and for embedding and preserving a wide variety of objects (Fig. 221). Polystyrene is an exceptionally clear material. It is also used to make innumerable household articles, including refrigerator parts, small radio cabinets, and wall tile.

The *polyvinyl plastics* are used in sheet form (Vinylite A, 1928), for waterproofing fabrics, in the manufacture of garden hose, and in the production of upholstery. During one month in 1947 over 400,000 pounds of polyvinyl acetate was blown into balloons by both children and adults. Polyvinyl plastics are not used extensively for molded objects.

The *polyacrylic esters* have many uses similar to those of polystyrene. The methyl methacrylate polymer is called Plexiglas (1936) and Lucite (1937), and in the form of molding compounds it is called both Lucite and Crystallite (1938). The acrylate plastics are used for coatings (Acrylate, 1931) and under the name of Plexigum (1931) for the manufacture of safety glass. Plexiglas has been used for windows and bubbles on bombers and other aircraft because it does not shatter, and it can be readily molded into almost any desired shape. When it becomes scratched, its surface can be made clear again simply by rubbing it with a cloth moistened with a solvent such as acetone.

Thermosetting Resins. The chemical difference between thermosetting resins and thermoplastic materials is that heating changes the molecular weight and chemical structure of the former and not of the latter. The thermoplastics generally have relatively long molecules with little cross linking, hence are plastic, while the thermosetting resins have higher molecular weights with many cross linkages, which account for their hardness and resistance to softening on heating. They are also much less soluble than the thermoplastics.

The *glyptal* (alkyd) resins are formed by the esterification of a polycarboxylic acid with a polyhydroxy alcohol. The acid ordinarily used is

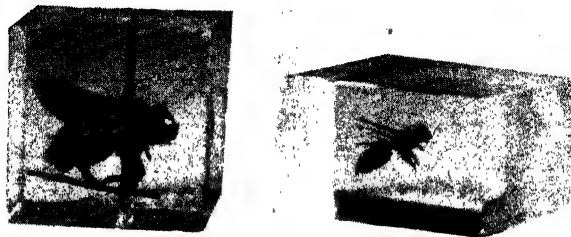


Figure 221. Insects imbedded in polystyrene (Styron). (Courtesy of The Dow Chemical Company.)



Figure 222. Polystyrene. (Courtesy of The Dow Chemical Company.)

phthalic acid, and the alcohol most frequently employed is glycerine. The glyptal resins are used as coating materials, as are most of the other synthetic resins.

The *phenol-formaldehyde resins* were the first to be manufactured

commercially (1909). They were developed by the American chemist Baekeland and were given the name Bakelite. Bakelite is a permanently hard, rigid, and infusible material that is resistant to chemicals and heat. It is usually formulated with a filler of wood pulp or similar material to make it less expensive. Bakelite is used for radio panels, phonograph records, pipestems, and insulators in electrical equipment and in many other places where its particular properties recommend its use.

Urea-formaldehyde and melamine-formaldehyde resins are similar in properties and uses to the phenol-formaldehyde resins. They are usually lighter in color and permit the use of pastel shades for boudoir accessories and radio cabinets, tableware, buttons, etc. The urea resin is widely used for laminations and the treatment of paper and cloth fabrics.

In 1947 over 850,000,000 pounds of plastic and resinous materials was produced. Of this amount, 236,000,000 pounds represented the production of thermosetting resins.

PAINT, VARNISH, AND LACQUER

It is fitting to complete this book with a discussion of paints, varnishes, and lacquers, for they represent familiar materials which are superficially simple but actually complex, the result of a blend of organic and inorganic chemistry with an assist from nature. The production of these materials is a billion-dollar-a-year industry.

Paint. Paints are mixtures of a number of organic and inorganic chemicals skillfully blended to give a product that, when spread on a surface, will dry to give a new surface that has a high covering capacity, will adhere firmly to the original surface, and will not discolor. The constituents of paints are usually listed under the following headings: pigment, vehicle, drier, thinner, and filler.

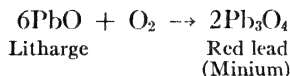
The *pigment* or pigments in a paint provide both the color and the hiding power, or opacity, of the paint. They also furnish durability to the finish, and they make a smooth, waxy surface as the paint dries. The choice of pigment frequently depends upon the atmospheric conditions to which the paint is to be exposed.

The chemistry of paint pigments is essentially the chemistry of the lead compounds, for a high percentage of the common pigments are lead derivatives. A few of the more important lead pigments are

White lead $\text{Pb}_2(\text{OH})_2\text{CO}_3$	(white)
Red lead Pb_3O_4	(red)
Lead chromate PbCrO_4	(yellow)
Basic lead chromate Pb_2OCrO_4	(orange)
Sublimed white lead (a mixture of PbSO_4 , PbO , and ZnO)	(white)
Sublimed blue lead (a mixture of PbSO_4 , PbSO_3 , PbS , ZnO , and C)	(blue)

By far the most widely used of these pigments is *white lead* (basic lead carbonate), which is used in nearly all paints regardless of color. It is produced by various processes, one of which consists in placing powdered lead in a large rotating wooden cylinder and moistening it with acetic acid. Hot air and carbon dioxide are then forced through the cylinders, and the basic lead carbonate forms. About 138,000,000 pounds of white lead was produced in 1947.

Red lead (minium) is prepared by heating litharge at 400°C .



Red lead has been used as a pigment for a great many years. Originally a "miniature" was a painting made using minium; only later did the meaning of small size become associated with this type of painting. Red lead was also used as the red pigment for illuminating manuscripts. At present it is used as the pigment in paints employed as rust-inhibiting coatings on structural steel. The 1947 production of red lead amounted to 68,800,000 pounds.

Lead chromate is brilliant yellow in color and is the commonest of the yellow pigments. Many shades of yellow can be obtained by modifying the procedure for the preparation of the lead chromate; for example, a lemon-yellow shade (*lemon chrome yellow*) is obtained by adding a small amount of sulfuric acid when the lead chromate is prepared. The change in color is caused by the presence of a small amount of white lead sulfate (PbSO_4). *Orange chrome yellow* results when sodium hydroxide is added during the preparation of the lead chromate. When Prussian blue and lead chromate are precipitated together, the product is *chrome-green pigment*. *Basic lead chromate* is

the very familiar orange pigment of highway and airway markers. It also gives its distinctive color to the Golden Gate Bridge in San Francisco, where it is used as the outer coating because of its brilliance and wearing qualities.

Sublimed white lead is used to some extent in place of white lead as a white pigment. It has better covering power than white lead, but it is



Figure 223. Many of the liquid raw materials of the paint, varnish, and lacquer industry are transported by tank car. (Courtesy of the Pittsburgh Plate Glass Co.)

more expensive. *Sublimed blue lead* is used in rust-inhibiting paint and has excellent covering power. It gets its color from the lead sulfide (black) and the carbon present.

There are a number of pigments comprising compounds of elements other than lead, the most important of which are titanium dioxide (TiO_2), zinc oxide (ZnO), and lithopone ($\text{BaSO}_4 + \text{ZnS}$). *Titanium dioxide* is used in small quantities in nearly all paints because it has the greatest hiding, or covering, power of any pigment. White lead, on the other hand, has the least covering power of any of the common pigments, but it is also the least expensive. The mixing of titanium dioxide and white lead results in an inexpensive paint with good covering power.

Zinc oxide (Fig. 224) is frequently used as the white pigment in paints

that come in contact with hydrogen sulfide. It is used under these conditions because zinc sulfide is white.

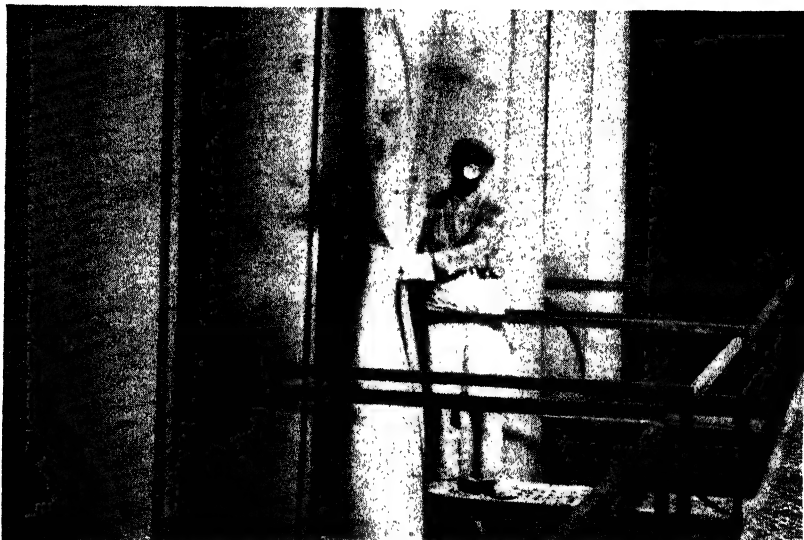
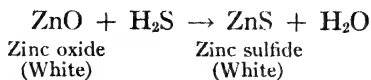
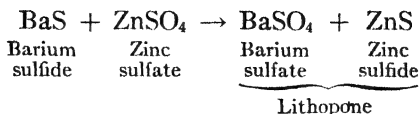


Figure 224. Collecting and loading zinc oxide. (Courtesy of The New Jersey Zinc Company.)

The cheaper lead pigments under the same conditions turn dark because of the formation of black lead sulfide. Zinc oxide is also used in house paint to combat mildew; very pure zinc oxide is the "Chinese white" used by artists.

Lithopone is an important white paint pigment prepared by a type of reaction, met with only infrequently, in which two soluble salts produce two insoluble ones.



The *vehicle* in a paint is the liquid material that upon exposure to air will oxidize and polymerize to form a hard, tenacious film on the coated

surface. This film serves both to protect the surface and to hold the pigment. Linseed oil is the most common vehicle, although tung oil and dehydrated castor oil are also widely used. These oils are characterized by their content of highly unsaturated molecules, and this gives them the ability to react with the oxygen in the air to form a



Figure 225. Steam-jacketed kettles used for the distillation of turpentine. (Courtesy of the Hercules Powder Co.)

horn-like substance. These oils are also called *drying oils*. *Driers* are metal oxides added to the paint to catalyze the oxidation and polymerization of the vehicle; they are usually oxides of manganese, cobalt, and nickel.

Thinners are inexpensive liquids added to make the paint thin (fluid) enough for easy application. Turpentine (Fig. 225) is the most popular thinner because of its marked solvent properties and low cost.

Fillers are inexpensive inert substances, such as gypsum, limestone, and barium sulfate, that are added to give the paint more "body" without materially increasing the price.

Varnish. The basic difference between paints and varnishes is that

varnishes do not contain either a pigment or a filler but have in their place a clear resin. Before the production of synthetic resins, the solid used in varnish consisted exclusively of natural resins from trees together with rosin from certain species of pine trees.

At present tung oil is the drying oil most frequently used for varnishes, and its use has made possible the "four-hour" varnishes. *Tung oil* comes from the nuts of the tung tree, which is native to

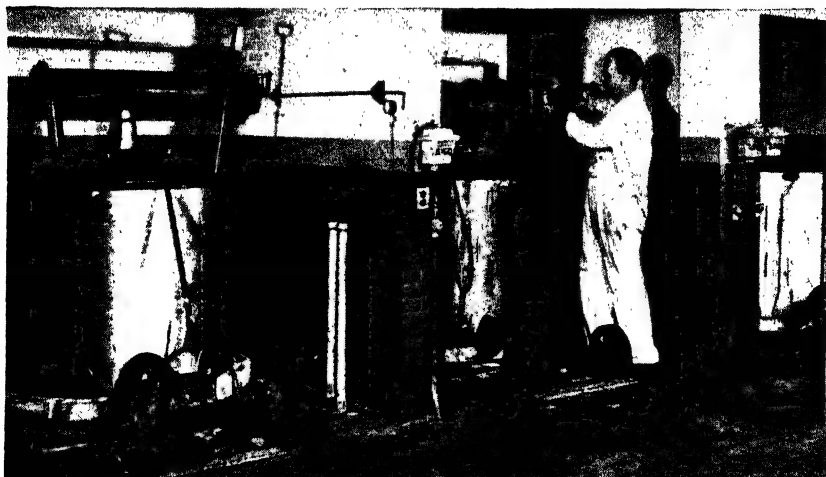


Figure 226. Portable kettles used for cooking varnish. (Courtesy of the Pittsburgh Plate Glass Co.)

China but is now grown extensively in the southern states. The remainder of the ingredients of varnish are similar to those in paints.

Lacquer. The term *lacquer* refers to finishes which contain pyroxylin or cellulose acetate and which dry as the result of the evaporation of an organic solvent and not as the result of a chemical reaction involving unsaturated compounds, as is the case with paints and varnishes. Lacquers are the most complex of the common coating agents since they contain (1) cellulose nitrate (pyroxylin) or acetate plastic, (2) a synthetic resin, (3) a plasticizer, (4) a solvent, (5) a diluent, and (6) a pigment (if it is an opaque lacquer).

The *synthetic resins* are added to give hardness and luster to the finished surface layer consisting of pyroxylin or cellulose acetate. The *plasticizers* are added to prevent cracking on drying, and the *solvents* are used to bring the resins and other coating materials into solution

to permit application. Several different solvents are used in each lacquer, and these are usually esters, alcohols, and ketones. High-boiling solvents are *n*-butyl acetate, *secondary*-butyl acetate, *n*-butyl alcohol, and methyl isobutyl ketone; medium-boiling solvents frequently used are methyl ethyl ketone (**MEK**) and ethyl acetate; low-boiling solvents are acetone, isopropyl alcohol, ethyl alcohol, and methyl alco-



Figure 227. Explosion and fire at Ludwigshafen, Germany, July 28, 1948, thought to have been caused by solvents. (Courtesy of Acme Newspictures.)

hol. The paint, varnish, and lacquer industry uses very large quantities of aliphatic organic chemicals, mostly as solvents (Fig. 227).

The *diluent* is used to dilute the mixture to give a consistency amenable to application by a spray gun and also to reduce the cost of the lacquer. The common diluents are aromatic hydrocarbons such as toluene or xylene. The *pigments* may be any of those used in paints.

EXERCISES

1. *New terms:* plastic, thermoplastic, plasticizer, varnish, vehicle, drier, drying oil, diluent, resin, thermosetting, paint, lacquer, pigment, thinner, filler.
2. Draw the structural formula of (a) tricresyl phosphate; (b) dibutyl phthalate; (c) *n*-butyl acetate; (d) methyl ethyl ketone.
3. What are the name and formula of a compound very frequently used in the preparation of thermosetting resins?
4. Name two places where it would be wise to use zinc oxide instead of white lead as the pigment in white paint. Explain.
5. How may thermoplastics be distinguished from thermosetting resins?
6. Indicate the contributions of each of the following to the paint and varnish industry: (a) inorganic chemistry; (b) organic chemistry; (c) nature.
7. What is the oldest synthetic plastic, and in what year was it first used?
8. Give an important general use for (a) synthetic resins and (b) thermoplastic materials.
9. In general, will a polymer with long-chain molecules and a small amount of cross linking between the molecules be harder than a polymer with many cross linkages?
10. Give the formulas of three compounds used as white pigments in paints. List these compounds in the descending order of their covering power.
11. In what way do paints differ from varnishes?
12. Make a list of all the articles made from plastics or containing plastics that are on your study desk.
13. What are the names of the five different types of materials in a paint?
14. Give a reason why titanium dioxide and white lead are used in colored paints.
15. What is the most widely used paint pigment?
16. Give the structural formula for each of three compounds used to make thermoplastics. What structural characteristic do these compounds have in common?

17. List five plastic articles commonly found in each of the main rooms of a house.
18. How many pounds of thermoplastics were produced in 1947?

COLLATERAL READING

- BARRON: "Modern Plastics," John Wiley & Sons, Inc., New York, 1946.
"Paint Power," distributed by the National Paint, Lacquer and Varnish Association, Washington, D.C., 1948.
RICHARDSON and WILSON: "Fundamentals of Plastics," McGraw-Hill Book Company, Inc., New York, 1946.
VON FISCHER: "Paint and Varnish Technology," Reinhold Publishing Corporation, New York, 1948.

Appendix

I. A SUMMARY OF UNITS OF MEASUREMENT

1. Length (distance)

A. The Metric System

By international agreement, the primary standard of length is the *meter*, and this is the distance (at 0°C.) between two lines on a certain metal bar made of the noble metals platinum and iridium. This is known as the *international prototype meter*, and the bar is kept at the International Bureau of Weights and Measures at Sèvres, France.

$$\begin{aligned}1 \text{ meter (m.)} &= 10 \text{ decimeters (dm.)} \\ &= 100 \text{ centimeters (cm.)} \\ &= 1000 \text{ millimeters (mm.)}\end{aligned}$$

$$1 \text{ kilometer (km.)} = 1000 \text{ meters}$$

B. The United States System and Some Metric-system Equivalents

In the United States system, the standard yard is defined as the 3600/3937 part of the meter.

$$\begin{aligned}1 \text{ yard (yd.)} &= 0.914402 \text{ meter} \\ &= 3 \text{ feet (ft.)} \\ &= 36 \text{ inches (in.)} \\ &= 0.181818 \text{ rod (rd.)}\end{aligned}$$

$$\begin{aligned}1 \text{ mile (mi.)} &= 5280 \text{ feet} \\ &= 320 \text{ rods} \\ &= 1.60935 \text{ kilometers}\end{aligned}$$

$$1 \text{ kilometer} = 0.62137 \text{ mile}$$

$$\begin{aligned}1 \text{ fathom} &= 6 \text{ feet} \\ &= 1.828804 \text{ meters}\end{aligned}$$

$$\begin{aligned}1 \text{ knot (or nautical mile)} &= 1.1516 \text{ statute miles} \\ &= 6080.27 \text{ feet} \\ &= 1.85325 \text{ kilometers}\end{aligned}$$

$$\begin{aligned}1 \text{ furlong} &= 660 \text{ feet} \\ &= 0.125 \text{ mile}\end{aligned}$$

$$1 \text{ mile} = 8 \text{ furlongs}$$

$$1 \text{ mil} = 0.001 \text{ inch}$$

2. Area*A. The United States System and Some Metric-system Equivalents*

1 acre (A.)	= 160 square rods (sq. rd.)
	= 4840 square yards (sq. yd.)
	= 43,560 square feet (sq. ft.)
	= 4046.873 square meters (sq. m.)
1 square mile (sq. mi.)	= 640 acres
	= 2.589998 square kilometers (sq. km.)

3. Weight (mass)*A. The Metric System*

The primary standard of mass is that of the *international prototype kilogram*. This is a body of platinum-iridium metal that is kept at the International Bureau of Weights and Measures. The mass of this particular object is equal to that of 0.001000027 cubic meter of pure water at 4°C. and 760 mm. pressure.

1 kilogram (kg.)	= 1000 grams (g.)
1 gram	= 10 decigrams (dg.)
	= 100 centigrams (cg.)
	= 1000 milligrams (mg.)

B. The United States System and Some Metric-system Equivalents

One pound avoirdupois is defined as the mass of 27.692 cubic inches of pure water weighed in air at 4°C. and 760 mm. pressure.

1 pound (lb.)	= 16 ounces (oz.)
	= 256 drams (dr.)
	= 7000 grains (gr.)
	= 0.005 short ton
	= 453.5924 grams
1 short ton	= 2000 pounds
1 long ton	= 1.12000 short tons
	= 2240 pounds
1 pound (avoirdupois)	= 1.21528 pounds (apothecaries')
1 pound (apothecaries')	= 12 ounces (oz. ap.)
	= 96 drams (dr. ap.)
	= 5760 grains
1 gram	= 15.432356 grains
	= 0.5643833 dr. av.
	= 0.03527396 oz. av.

4. Volume*A. The Metric System*

1 cubic meter (cu.m.) = 1,000,000 cubic centimeters (cc.)

1 cubic centimeter = 1000 cubic millimeters (cu.m.)

B. The United States System and Some Metric-system Equivalents

1 cubic yard (cu. yd.) = 27 cubic feet (cu. ft.)

1 cubic foot = 1728 cubic inches (cu. in.)

1 cubic inch = 16.387 cubic centimeters

1 cubic meter = 35.315 cubic feet

1 cubic centimeter = 0.061 cubic inch

1 cord = 128 cubic feet

5. Capacity*A. The Metric System*

1 liter (l.) = 1000 milliliters (ml.)

= 1000.027 cubic centimeters

1 milliliter = 1.000027 cubic centimeters

1 kiloliter (kl.) = 1000 liters

*B. The United States System and Some Metric-system Equivalents**Liquid measure:*

1 gallon (gal.) = 4 quarts (qt.)

= 3.785332 liters

1 quart = 57.75 cubic inches

= 0.946333 liter

1 liter = 1.05671 quart

10 liters = 2.64178 United States gallons

= 2.200 British Imperial gallons

Apothecaries' fluid measure:

1 fluid ounce (fl. oz.) = 8 fluid drams (fl. dr.)

= 0.625 pint

= 29.5729 milliliters

Dry measure:

1 bushel (bu.) = 4 pecks (pk.)

= 32 quarts

= 35.2383 liters

1 quart = 67.200625 cubic inches

= 1.101198 liters

1 liter = 0.9081 quart

II. THE CHEMICAL ELEMENTS

<i>Element</i>	<i>Symbol</i>	<i>Atomic number</i>	<i>Atomic weight</i>	<i>Physical state*</i>
Hydrogen	H	1	1.0080	Gas
Helium	He	2	4.003	Gas
Lithium	Li	3	6.940	Solid
Beryllium	Be	4	9.02	Solid
Boron	B	5	10.82	Solid
Carbon	C	6	12.010	Solid
Nitrogen	N	7	14.008	Gas
Oxygen	O	8	16.0000	Gas
Fluorine	F	9	19.00	Gas
Neon	Ne	10	20.183	Gas
Sodium	Na	11	22.997	Solid
Magnesium	Mg	12	24.32	Solid
Aluminum	Al	13	26.97	Solid
Silicon	Si	14	28.06	Solid
Phosphorus	P	15	30.98	Solid
Sulfur	S	16	32.066	Solid
Chlorine	Cl	17	35.457	Gas
Argon	A	18	39.944	Gas
Potassium	K	19	39.096	Solid
Calcium	Ca	20	40.08	Solid
Scandium	Sc	21	45.10	Solid
Titanium	Ti	22	47.90	Solid
Vanadium	V	23	50.95	Solid
Chromium	Cr	24	52.01	Solid
Manganese	Mn	25	54.93	Solid
Iron	Fe	26	55.84	Solid
Cobalt	Co	27	58.94	Solid
Nickel	Ni	28	58.69	Solid
Copper	Cu	29	63.54	Solid
Zinc	Zn	30	65.38	Solid
Gallium	Ga	31	69.72	Solid
Germanium	Ge	32	72.60	Solid
Arsenic	As	33	74.91	Solid
Selenium	Se	34	78.96	Solid
Bromine	Br	35	79.916	Liquid
Krypton	Kr	36	83.7	Gas
Rubidium	Rb	37	85.48	Solid
Strontium	Sr	38	87.63	Solid
Yttrium	Y	39	88.92	Solid
Zirconium	Zr	40	91.22	Solid
Columbium	Cb	41	92.91	Solid
Molybdenum	Mo	42	95.95	Solid
Technetium	Tc	43	Solid

* The state in which the element exists under ordinary atmospheric conditions.

<i>Element</i>	<i>Symbol</i>	<i>Atomic number</i>	<i>Atomic weight</i>	<i>Physical state*</i>
Ruthenium	Ru	44	101.7	Solid
Rhodium	Rh	45	102.91	Solid
Palladium	Pd	46	106.7	Solid
Silver	Ag	47	107.880	Solid
Cadmium	Cd	48	112.41	Solid
Indium	In	49	114.76	Solid
Tin	Sn	50	118.70	Solid
Antimony	Sb	51	121.76	Solid
Tellurium	Te	52	127.61	Solid
Iodine	I	53	126.92	Solid
Xenon	Xe	54	131.3	Gas
Cesium	Cs	55	132.91	Solid
Barium	Ba	56	137.36	Solid
Lanthanum	La	57	138.92	Solid
Cerium	Ce	58	140.13	Solid
Praseodymium	Pr	59	140.92	Solid
Neodymium	Nd	60	144.27	Solid
		61	Solid
Samarium	Sm	62	150.43	Solid
Europium	Eu	63	152.0	Solid
Gadolinium	Gd	64	156.9	Solid
Terbium	Tb	65	159.2	Solid
Dysprosium	Dy	66	162.46	Solid
Holmium	Ho	67	164.94	Solid
Erbium	Er	68	167.2	Solid
Thulium	Tm	69	169.4	Solid
Ytterbium	Yb	70	173.04	Solid
Lutecium	Lu	71	174.99	Solid
Hafnium	Hf	72	178.6	Solid
Tantalum	Ta	73	180.88	Solid
Tungsten	W	74	183.92	Solid
Rhenium	Re	75	186.31	Solid
Osmium	Os	76	190.2	Solid
Iridium	Ir	77	193.1	Solid
Platinum	Pt	78	195.23	Solid
Gold	Au	79	197.2	Solid
Mercury	Hg	80	200.61	Liquid
Thallium	Tl	81	204.39	Solid
Lead	Pb	82	207.21	Solid
Bismuth	Bi	83	209.00	Solid
Polonium	Po	84	210	Solid
Astatine	At	85	Solid
Radon	Rn	86	222	Gas

* The state in which the element exists under ordinary atmospheric conditions.

II. THE CHEMICAL ELEMENTS (*Continued*)

<i>Element</i>	<i>Symbol</i>	<i>Atomic number</i>	<i>Atomic weight</i>	<i>Physical state*</i>
Francium	Fa	87	Solid
Radium	Ra	88	226.05	Solid
Actinium	Ac	89	227.05	Solid
Thorium	Th	90	232.12	Solid
Protoactinium	Pa	91	231	Solid
Uranium	U	92	238.07	Solid
Neptunium	Np	93	Solid
Plutonium	Pu	94	Solid
Americium	Am	95	Solid
Curium	Cm	96	Solid

* The state in which the element exists under ordinary atmospheric conditions.

III. VAPOR PRESSURE OF WATER*

<i>Temperature, degrees centigrade</i>	<i>Pressure, millimeters</i>	<i>Temperature, degrees centigrade</i>	<i>Pressure, millimeters</i>
0	4.580	31	33.662
5	6.536	32	35.629
10	9.197	33	37.695
15	12.771	34	39.863
16	13.617	35	42.139
17	14.511	36	44.527
18	15.457	40	55.288
19	16.456	45	71.840
20	17.512	50	91.492
21	18.626	55	118.03
22	19.803	60	149.38
23	21.043	65	187.56
24	22.351	70	233.71
25	23.728	75	289.12
26	25.181	80	355.22
27	26.709	85	433.56
28	28.318	90	525.86
29	30.011	95	634.00
30	31.791	100	760.00

* Osborne and Myers, *National Bureau of Standards Journal of Research*, **18**, 11 (1934).

IV. COMMON NAMES OF CHEMICALS

<i>Common name</i>	<i>Chemical name</i>	<i>Formula</i>
Agate	Silicon dioxide	SiO ₂
Alabaster	Calcium sulfate	CaSO ₄ ·2H ₂ O
Alcohol	Ethyl alcohol	CH ₃ CH ₂ OH
Alum	Potassium aluminum sulfate	KAl(SO ₄) ₂ ·12H ₂ O
Alundum	Aluminum oxide	Al ₂ O ₃
ANTU	<i>Alpha</i> -naphthylthiourea	
Aqua ammonia	Ammonium hydroxide	NH ₄ OH
Aqua fortis	Nitric acid	HNO ₃
Aqua regia	Mixture of concentrated HCl and concentrated HNO ₃	
Aspirin	Acetyl salicylic acid	
Benzol	Benzene	C ₆ H ₆
Bleaching powder	Calcium chloride hypochlorite	CaOCl ₂
Blue vitriol	Copper sulfate	CuSO ₄ ·5H ₂ O
Bluing	Ferric ferrocyanide	Fe ₃ [Fe(CN) ₆] ₃
Boracic acid	Boric acid	H ₃ BO ₃
Borax	Sodium tetraborate	Na ₂ B ₄ O ₇ ·10H ₂ O
Brimstone	Sulfur	S
Burnt alum	Potassium aluminum sulfate	KAl(SO ₄) ₂
Calomel	Mercurous chloride	Hg ₂ Cl ₂
Carbide	Calcium carbide	CaC ₂
Carbolic acid	Phenol	C ₆ H ₅ OH
Caustic potash	Potassium hydroxide	KOH
Caustic soda	Sodium hydroxide	NaOH
Chalk	Calcium carbonate	CaCO ₃
Chloride of lime	Calcium chloride hypochlorite	CaOCl ₂
Chrome green	Chromium trioxide	Cr ₂ O ₃
Chrome yellow	Lead chromate	PbCrO ₄
Copperas	Ferrous sulfate	FeSO ₄ ·7H ₂ O
Corrosive sublimate	Mercuric chloride	HgCl ₂
Dextrose	Glucose	C ₆ H ₁₂ O ₆
DDT	Dichlorodiphenyltrichloroethane	
Ether	Diethyl ether	CH ₃ CH ₂ OCH ₂ CH ₃
Fool's gold	Iron disulfide	FeS ₂
Flint	Silicon dioxide	SiO ₂
Freon	Dichlorodifluoromethane	CCl ₂ F ₂
Glauber's salt	Sodium sulfate	Na ₂ SO ₄ ·10H ₂ O
Glycerine	Glycerol	CH ₂ OHCHOHCH ₂ OH
Grain alcohol	Ethyl alcohol	CH ₃ CH ₂ OH
Green vitriol	Ferrous sulfate	FeSO ₄ ·7H ₂ O
Gypsum	Calcium sulfate	CaSO ₄ ·2H ₂ O
Hypo	Sodium thiosulfate	Na ₂ S ₂ O ₃ ·5H ₂ O
Irium	Sodium lauryl sulfate	C ₁₂ H ₂₅ OSO ₃ Na
Javelle water	Sodium hypochlorite solution	NaOCl

<i>Common name</i>	<i>Chemical name</i>	<i>Formula</i>
Laughing gas	Nitrous oxide	N_2O
Levulose	Fructose	$C_6H_{12}O_6$
Litharge	Lead monoxide	PbO
Lunar caustic	Silver nitrate	$AgNO_3$
Lye	Sodium hydroxide	$NaOH$
Marble	Calcium carbonate	$CaCO_3$
Marsh gas	Methane	CH_4
Milk of lime	Calcium hydroxide solution	$Ca(OH)_2$
Milk of magnesia	Magnesium hydroxide sus- pended in water	$Mg(OH)_2$
Moth balls	Naphthalene	$C_{10}H_8$
Muriatic acid	Impure hydrochloric acid	HCl
Niter	Potassium nitrate	KNO_3
Nitroglycerine	Glyceryl trinitrate	
Oil of bitter almonds	Benzaldehyde	C_6H_5CHO
Oil of vitriol	Concentrated sulfuric acid	H_2SO_4
Oil of wintergreen	Methyl salicylate	
Oleum	Fuming sulfuric acid	$H_2SO_4 + SO_3$
Paris green	Double salt of copper acetate and copper arsenite	$Cu(C_2H_3O_2)_2 \cdot Cu_3(AsO_3)_2$
Peroxide	Hydrogen peroxide solution	H_2O_2
Plaster of Paris	Calcium sulfate	$(CaSO_4)_2 \cdot H_2O$
Potash	Potassium carbonate	K_2CO_3
Prussian blue	Ferric ferrocyanide	$Fe_4[Fe(CN)_6]_3$
Prussic acid	Hydrocyanic acid	HCN
Quicksilver	Mercury	Hg
Red lead	Lead orthoplumbate	Pb_3O_4
Rochelle salt	Potassium sodium tartrate	$KNaC_4H_4O_6$
Rock salt	Sodium chloride	$NaCl$
Rouge	Ferric oxide	Fe_2O_3
Sal ammoniac	Ammonium chloride	NH_4Cl
Sal soda	Sodium carbonate	$Na_2CO_3 \cdot 10H_2O$
Salt cake	Impure sodium sulfate	Na_2SO_4
Saltpeter	Potassium nitrate	KNO_3
Soda ash	Sodium carbonate	Na_2CO_3
Sugar	Sucrose	$C_{12}H_{22}O_{11}$
Sugar of lead	Lead acetate	$Pb(C_2H_3O_2)_2 \cdot 3H_2O$
1080	Sodium monofluoroacetate	CH_2FCO_2Na
TNT	Trinitrotoluene	
Toluol	Toluene	$C_6H_5CH_3$
Turnbull's blue	Ferrous ferricyanide	$Fe_3[Fe(CN)_6]_2$
2,4-D	2,4-Dichlorophenoxyacetic acid	
Verdigris	Basic copper acetate	$Cu(OH)C_2H_3O_2$
Vermilion	Mercuric sulfide	HgS
White arsenic	Arsenious oxide	As_2O_3
White lead	Basic lead carbonate	$Pb_2(OH)_2CO_3$
Wood alcohol	Methyl alcohol	CH_3OH

V. ANSWERS TO EXERCISES

Chapter 4

7. (a) 8.0165
(b) 0.2520
14. (a) 394.768
(b) 222.29
(c) 380.58
16. (a) 80.3%
(b) 7.2%
(c) 63.5%
(d) 60.4%
18. (a) 3.9 lb.
(b) 0.8 lb.
(c) 1.9 lb.
19. 6.3 g.

Chapter 7

18. 250 mm.

Chapter 8

9. 53.6°F.
10. 5 cc.
11. 172.1 cc.
12. 769.5 cc.
13. 745.5 cc.

Chapter 11

14. (a) 31.3 lb.
(b) 48.7 lb.
15. 4.8 tons

Chapter 13

12. 9.03×10^{23}
13. -0.19°C .
14. (a) 360 g.
(b) 18 g.
(c) 75.6 g.
15. 0.006 g.

Chapter 15

10. 6 N
11. 3.2 g.
12. 56.1 g.

Chapter 18

16. 46,575,342

Chapter 19

21. 8,350,000 oz.

Chapter 20

21. 41.7% (usually 42%)

Chapter 21

17. 75 tons of scrap
15 tons of limestone

Chapter 22

23. 1,125,000 tons

Chapter 23

19. \$1,814,400

Chapter 24

16. 7,500,000

Chapter 25

20. 74% "isooctane,"
26% *n*-heptane
21. 2.84 miles
22. 226.6 gal.

Chapter 26

16. 213,333,333 lb.

Chapter 27

17. About 18 lb.
18. About 41.4 lb.

Chapter 29

19. 11.6 billion pounds
21. 91.25 lb.

Chapter 30

18. About 3.6 cents

Chapter 31

20. 1.1 cents
21. 4,120,248 tons

Chapter 32

18. 614,000,000

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